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DEBYE CHARACTERISTIC TEMPERATURE OF CUBIC METALS

and

VIBRATION SPECTRUM AND SPECIFIC HEAT OF SILVER

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
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by

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ABSTRACT

An approximation to the Debye characteristic temperature at 0 °K is developed and applied to several cubic metals. The results obtained are estimated to be accurate to better than 1%.

In addition, the Born and Begbie theory of lattice vibrations is applied to the calculation of the specific heat and Debye temperature of silver over the temperature range 0° - 150°K. Three such calculations were carried out; the Houston approximation to the frequency spectrum used in the first calculation is extended in the second calculation to take into account the variation with temperature of the elastic constants, and is modified in the third calculation so as to give the correct results at both low and high temperatures. The results agree with experiment to approximately the same degree as the similar calculations of Bhatia and Horton on the basis of the Bhatia theory.

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INTRODUCTION

The subject matter divides naturally into three fairly well-defined regions of discussion and is so treated. In Part I, after an outline of the historical development of specific heat theory, a general expression for specific heats is derived and is discussed at some length. An accurate approximation to the Debye characteristic temperature, Θ_D, of cubic metals at $0^\circ K$ is developed in Part II and is applied to the calculation of Θ_D of several common metals. In Part III Born and Begbie's theory of lattice vibrations[1] is applied to the calculation of the specific heat of silver. Three calculations of this type are carried out, with an attempt in two of them to take into consideration the variation with temperature of the elastic constants. The results are compared with experiment and with similar calculations by Bhatia and Horton[2] based on the Bhatia theory of lattice-conduction electron interactions in monovalent cubic metals[3].

PART I. HISTORICAL DEVELOPMENT OF SPECIFIC HEAT THEORY

Classical Theory

On the basis of classical statistical mechanics, the energy of an oscillator moving under harmonic, i.e. linear, forces is KT per degree of freedom, where K is the Boltzmann constant and T is the absolute temperature. Since there are three degrees of freedom for each particle, the internal energy U of a system of N particles is given by

$$U = 3NKT. \tag{1}$$

The heat capacity at constant volume, C_v, is obtained by taking the derivative of the internal energy with respect to temperature. Thus

$$C_v = 3NK. \tag{2}$$

This is in reasonably good agreement with experiment at high temperatures but fails completely at low temperatures where C_v falls to low values. The introduction of quantum theory corrects this situation.

Energy and Heat Capacity of a System of Harmonic Oscillators - Quantum Theory

An elementary result of quantum theory is that the energy of a one-dimensional harmonic oscillator is given by

$$W_n = (n + \tfrac{1}{2})\hbar\omega \tag{3}$$

where $\hbar$ is Planck's constant divided by 2π,

ω is the angular frequency of vibration, and

n is the quantum state of the oscillator.

The probability that a given oscillator in thermal equilibrium will be in state n (energy state W_n) is

(4) $$e^{-W_n/KT} = e^{-(n + \frac{1}{2})\hbar\omega/KT} .$$

The average energy $\overline{W}_n$ of such an oscillator is

(5) $$\overline{W}_n = \frac{\sum_{n=o}^{\infty} W_n e^{-W_n/KT}}{\sum_{n=o}^{\infty} e^{-W_n/KT}}$$

$$= \frac{\hbar\omega \sum_{n=o}^{\infty} (n + \frac{1}{2}) e^{-(n + \frac{1}{2})\hbar\omega/KT}}{\sum_{n=o}^{\infty} e^{-(n + \frac{1}{2})\hbar\omega/KT}}$$

$$= \frac{1}{2} \hbar\omega + \hbar\omega /(e^{\hbar\omega/KT} - 1) .$$

For high temperatures $(\hbar\omega \ll KT)$, the expression reduces to the classical result $\overline{W}_n = KT$.

The internal energy of a system of N such oscillators, each with three degrees of freedom is

(6) $$U = 3N W_n$$
$$= (3/2)\hbar\omega + 3N \hbar\omega/(e^{\hbar\omega/KT} - 1) .$$

Differentiation of (6) with respect to T gives the heat capacity

(7) $$C_v = \frac{3N (\hbar\omega)^2 e^{\hbar\omega/KT}}{KT^2 (e^{\hbar\omega/KT} - 1)^2}$$
$$= 3NK \; x^2 e^x /(e^x - 1)^2$$
$$= 3NK \; E(x)$$

where $x = \hbar\omega/KT$, and

$E(x) = x^2 e^x /(e^x - 1)^2$ is the Einstein function.

It was proposed by Einstein[4] to use this expression for C_v as an approximation to the entire heat capacity of a solid. At high temperatures $(x \rightarrow 0)$, $E(x)$ approaches 1 and C_v goes to $3NK$, the classical result. At low temperatures $E(x)$, and hence C_v, fall to low values. Though the result is qualitatively correct, it fails to give correctly the details of the approach of C_v to zero.

Frequency Distribution Function

It is necessary to replace the single frequency used in the Einstein theory by a range of frequencies, characteristic of the substance, whose individual contributions to the specific heat are expressed in a freqency distribution function $G(\omega)d\omega$, the number of frequencies lying between ω and $\omega + d\omega$. The internal energy is then given by

$$(8) \qquad U = \int G(\omega)\hbar\omega(e^{\hbar\omega/KT} - 1)^{-1}d\omega$$

with the condition that

$$(9) \qquad V \int G(\omega)d\omega = 3N_0V$$

where $3N_0V$ is the total number of modes of vibration in volume V, and N_0 is the number of atoms per unit volume.

Differentiation of (8) with respect to T leads to the general expression for the specific heat c_v per atom at constant volume

$$(10) \qquad N_0Vc_v = K(\hbar/KT)^2 \int G(\omega)\omega^2 e^{\hbar\omega/KT} (e^{\hbar\omega/KT} - 1)^{-2}d\omega$$

Determination of $G(\omega)$

Consider a cube of side L. The condition that a vibration wave $e^{i\underline{k}\cdot\underline{r}}$ be periodic within the cube is that there be an integral number of wavelengths λ between the ends of the cube. Since $k = 2\pi/\lambda$, the necessary condition for periodicity becomes that k_xL, k_yL, and k_zL be

multiples of 2π. The allowed values of the wave-vector k may be represented by the points of a simple cubic lattice in k-space with lattice constant $2\pi/L$. The number of points in an element of k-space $dk_x dk_y dk_z$ is

$$\frac{dk_x dk_y dk_z}{(2\pi/L)^3} = \frac{V}{(2\pi)^3} dk_x dk_y dk_z . \tag{11}$$

In polar co-ordinates, the element of volume in k-space is given by $k^2 dk d\Omega$, where $d\Omega$ is an element of solid angle. The number of modes between k and k + dk in a solid angle $d\Omega$, $N(k)dkd\Omega$, is

$$\begin{aligned} N(k)dkd\Omega &= \frac{V}{(2\pi)^3} k^2 dk d\Omega \\ &= \frac{V}{(2\pi)^3} k^2 \frac{dk}{d\omega} d\omega d\Omega \\ &= g'(\omega) d\omega d\Omega \end{aligned} \tag{12}$$

since k is a function of ω. Waves of a given k occur with three different polarisations (one longitudinal and two transverse), so that

$$g(\omega) = \frac{V}{(2\pi)^3} \sum_{i=1}^{3} k^2(\omega_i) \frac{dk(\omega_i)}{d\omega_i} \tag{13}$$

The required frequency distribution function $G(\omega)d\omega d\Omega$ is obtained by integrating (13) over all solid angles, giving

$$VG(\omega)d\omega = \frac{V}{(2\pi)^3} d\omega \int \sum_{i=1}^{3} k^2(\omega_i) \frac{dk(\omega_i)}{d\omega_i} d\Omega . \tag{14}$$

Thus, on the basis of a given model, $G(\omega)$ can be determined in principle from the dispersion (ω vs. k) relations.

Debye Approximation

If the solid is regarded as continuous, then

(15) $$\omega_i = v_i k$$

where the velocity of the wave v_i is, in general, a function of direction. $G(\omega)$ becomes

(16) $$G(\omega)\ d\omega = (1/2\pi)^3 \omega^2 d\omega \int \sum_{i=1}^{3} d\Omega / v_i^3(\theta,\varphi)$$
$$= \alpha_1 \omega^2 d\omega$$

with

(17) $$\alpha_1 = (1/2\pi)^3 \int \sum_{i=1}^{3} d\Omega / v_i^3(\theta,\varphi).$$

Since $G(\omega)d\omega = \alpha_1 \int \omega^2 d\omega$ would be infinite if ω were allowed to assume all values, we require that there be a cut-off frequency ω_m such that

(18) $$G(\omega)d\omega = \alpha_1 \omega^2 d\omega \qquad \text{for } \omega \leq \omega_m ,$$
$$= 0 \qquad \text{for } \omega \geq \omega_m .$$

The maximum frequency is fixed by the requirement that $\int G(\omega)d\omega = 3N_o$. Therefore

(19) $$\omega_m = (9N_o/\alpha_1)^{1/3}.$$

Introducing (16) for $G(\omega)$ in (10), replacing α_1 by $9N_o/\omega_m^3$ and $\hbar\omega/KT$ by x, and rearranging, one obtains

(20) $$N_o V c_v = 9 N_o V K (KT/\hbar\omega)^3 \int_0^{x_m} x^2 E(x) dx.$$

Since $\hbar\omega/K$ has the dimensions of temperature, we can write

(21) $$\theta_D = \hbar\omega_m/K.$$

This is the definition of the Debye characteristic temperature. (20), written in terms of θ_D, becomes

(22) $$c_v = 9K(T/\theta_D)^3 D(\theta_D/T)$$

where

(23) $$D(\theta_D/T) = \int_0^{\theta_D/T} x^2 E(x)\,dx\,.$$

Low Temperature Behaviour of Debye Approximation to c_v

As $T \rightarrow 0$, $\theta_D/T \gg 1$, and the upper limit of integration in $D(\theta_D/T)$ may be taken as infinity.

(24) $$D(\theta_D/T)_{T\rightarrow 0} = \int_0^{\infty} x^4 e^x (e^x - 1)^{-2} dx.$$

Consider the integral

(25) $$\begin{aligned} I &= \int_0^{\infty} x^3 (e^x - 1)^{-1} dx \\ &= \frac{1}{4}\,\frac{x^4}{e^x - 1}\Big|_0^{\infty} + \frac{1}{4}\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \\ &= \frac{1}{4}\,D(\theta_D/T). \end{aligned}$$

Now

(26) $$\begin{aligned} \int_0^{\infty} \frac{x^3 dx}{e^x - 1} &= \int_0^{\infty} \frac{x^3 e^{-x}}{1 - e^{-x}}\,dx \\ &= \int_0^{\infty} x^3 \Big(\sum_{n=1}^{\infty} e^{-nx} \Big) dx \\ &= \sum_{n=1}^{\infty} 6/n^4 \\ &= \pi^4/15. \end{aligned}$$

Therefore $D(\infty) = 4\pi^4/15$

and

(27) $$c_{v\ T\rightarrow 0} = 9K(T/\theta_D)^3\ 4\pi^4/15.$$

Thus at low temperatures, c_v obeys a T^3 law.

Failure of Debye Approximation

The range of validity of (27) is, unfortunately, not too great. The limit on the usefulness is set, not by mathematics, but by physical

reality. The Debye approximation just does not represent the true picture. For instance, since $\Theta_D = \hbar\omega_m/K = (9N_o/\alpha_1)^{1/3}\hbar/K$, Θ_D should be independent of temperature. However, if one substitutes actual c_v's into (22), one obtains a Θ_D which is not constant with temperature, but exhibits a minimum. The reason for the failure of the Debye theory is, of course, due to the neglect of the discrete structure of matter. Since the advent of the Debye theory, more elaborate treatments of specific heats have arisen, which take into account the atomic nature of matter.

Born - von Karman Theory

Until recently, it has been customary to determine the frequency distribution on the basis of the Born - von Karman model[5], assuming central Hooke's Law forces between an atom and its nearest and next nearest neighbours. This introduces two unknown force constants which are then determined by the requirement that the velocities of long elastic waves as determined from elasticity theory, and expressed in terms of the elastic constants, correspond to the velocities as obtained from the microscopic theory. There are, in general, three independent elastic constants for cubic crystals (c_{11}, c_{12}, and c_{44}). One relation between the elastic constants exists if either the crystal is elastically isotropic ($2c_{44} = c_{11} - c_{12}$), or the entire interactions are central and the Cauchy relation is satisfied ($c_{12} = c_{44}$). Unfortunately, in metals this is seldom the case. Hence, one may use an approximation, introduced by Fine[6], by means of which the three elastic constants are reduced to two independent ones.

Bhatia Theory

More recently, Bhatia[3] has developed a new theory, taking the conduction electrons into account in an approximate way. This introduces a non-central component into the interactions and yields three atomic force constants which can be uniquely related to the three independent elastic constants.

Born and Begbie Theory

In 1947, Born and Begbie[1] extended the Born - von Karman model to include non-central forces (general forces) and it is this theory which will be applied here to the calculation of the specific heat of silver. If one applies the Born and Begbie theory to face-centered cubic crystals, such as silver, one finds that the nearest neighbours introduce three force constants which can be uniquely determined in terms of the three elastic constants.

Secular Equation for the Frequencies

On the basis of the Born and Begbie theory of lattice vibrations, the secular equation for the frequencies is

(28) $$\left| D_{ij}\,(k) - \omega^2 I_{ij} \right| = 0$$

where $D_{ii} = (4/a^2\rho)\left\{ \alpha + 2\beta - \alpha C_{jk} - \beta(C_{ij} + C_{ki}) \right\}$

$D_{ij} = (4\gamma/a^2\rho) S_i S_j$

$I_{ij} = 1$ for $i = j$,

$= 0$ for $i \neq j$,

and $C_{ij} = \cos(ak_i/\sqrt{2})\cos(ak_j/\sqrt{2})$

$S_i = \sin(ak_i/\sqrt{2})$.

'a' is the nearest neighbour distance and the force constants and elastic

constants are related in the following way:

$$\alpha = c_{44} - c_{11}/2 \tag{29}$$

$$\beta = c_{11}/2$$

$$\gamma = (c_{11} - c_{44} - \epsilon)/2$$

with $\epsilon = c_{11} - c_{12} - 2c_{44}$

The secular equation (28) has three solutions of ω^2 for a given $\underline{k}$ direction, corresponding to one longitudinal and two transverse branches. However, we should note that only in certain special directions are the solutions purely longitudinal and transverse.

PART II. DEBYE Θ_D AT LOW TEMPERATURES

Validity of Debye Approximation at Low Temperatures

We have found, using the Debye approximation, that

(1) $$\Theta_D = (9N_0/\alpha_1)^{1/3}\hbar/K .$$

This expression can be used to calculate Θ_D at temperatures near 0°K, since only the lowest frequencies, or equivalently, the longest wavelengths, are excited in this temperature region. The lattice structure of the metal is not apparent to long waves, so that a continuous medium approximation is applicable.

Approximations to α_1

We now proceed with the evaluation of α_1, which is given by (I.17) as

(2) $$\alpha_1 = (1/2\pi)^3 \int \sum_{i=1}^{3} d\Omega/v_i^3 .$$

Since crystals in general are not isotropic, the v_i depend on direction in a complicated way, with the result that the integral must be evaluated by approximate methods. Several such methods have been devised and we shall discuss some of them in greater or lesser detail.

Hopf - Lechner Approximation

Until recently, a method often used has been that of Hopf and Lechner[7]. The integral (2) is evaluated by expanding the integrand in a polynomial in v_i^2 and determining the coefficients by the Lagrange interpolation method. Two of the defects of this approach are that the method is extremely labourious and that there is no means of ascertaining the accuracy of the result.

Quimby - Sutton Approximation

A modification of the Hopf - Lechner method is that of Quimby and Sutton[8]. It is based upon an evaluation of the distribution in solid angle of the roots of the cubic equation which describes the propagation of acoustic waves in the crystal. The authors claim an uncertainty in the computed value of Θ_D due to the approximation of the order of 0.1% when the anisotropy factor $\eta = 2c_{44}/(c_{11} - c_{12})$ is as large as 4. The method does appear to involve a considerable amount of work.

Blackman Approximation

A very simple semi-theoretical formula for Θ_D, designed to cover cases where η is considerably greater than 1, has been developed by Blackman[9]. Calculations can be quickly made with the formula to an accuracy of 5 - 10%.

Bhatia - Tauber Approximation

More recently, a simple approximate expression for the integral (2) was derived by Bhatia and Tauber[10], based on a method employed by Houston[11] to obtain the approximate form for the frequency spectrum of crystals. The integrand is expanded in those Kubic Harmonics K_m, first introduced by von der Lage and Bethe[12], which are invariant under the operations of the cubic symmetry group. Thus

$$(3) \qquad \alpha_1 = (1/2\pi)^3 \int \left[\sum_{m=0}^{\infty} \beta_m K_m \right] d\Omega .$$

Since

$$(4) \qquad \int K_m d\Omega = 0 \qquad m \neq 0$$

$$= 4\pi \qquad m = 0$$

we have

$$(5) \qquad \alpha_1 = (1/2\pi)^3 4\pi\beta_0.$$

If the crystal is not too anisotropic, the first three Kubic Harmonics are sufficient to give a good approximation to the integral. In terms of the direction cosines x, y, z,

$$(6) \qquad \begin{aligned} K_0 &= 1 \\ K_1 &= x^4 + y^4 + z^4 - 3/5 \\ K_2 &= x^2y^2z^2 + (1/22)K_1 - 1/105 \end{aligned}$$

The coefficients β_0, β_1, and β_2 are determined analytically from the solutions of the secular equation (I.28) along the three principal directions of a cubic crystal, (100), (110), and (111). The quantities referring to these three directions will be distinguished by the subscripts A, B, and C, respectively. β_0 is then given by

$$(7) \qquad \beta_0 = (1/35)\sum_{i=1}^{3}\left\{10(1/v_i^3)_A + 16(1/v_i^3)_B + 9(1/v_i^3)_C\right\}.$$

Therefore,

$$(8) \qquad \alpha_1 = (1/2\pi)^3(4\pi/35)\sum_{i=1}^{3}\left\{10(1/v_i^3)_A + 16(1/v_i^3)_B + 9(1/v_i^3)_C\right\}.$$

A better approximation to α_1 can be obtained by using more terms in the expansion in Kubic Harmonics. By taking three more directions, (210), (211), and (221), denoted by D, E, and F, respectively, Betts, Bhatia, and Wyman[13] have derived the following six-term approximation to α_1:

$$\begin{aligned} (9) \qquad \alpha_1 = (1/2\pi)^3(4\pi/1{,}081{,}080)\sum_{i=1}^{3}\Big\{&117{,}603(1/v_i^3)_A + 76{,}544(1/v_i^3)_B \\ &+ 17{,}496(1/v_i^3)_C + 381{,}250(1/v_i^3)_D + 311{,}040(1/v_i^3)_E + \\ &177{,}147(1/v_i^3)_F\Big\}. \end{aligned}$$

A more complete discussion on Kubic Harmonics and their properties will be found in Ref. 13.

Schiff Approximation

At the suggestion of Dr. Schiff, the above approximations may be improved up on in the following way.

On expanding the determinant (I.28), one obtains a cubic in ω^2

(10) $$\omega^6 + a\omega^4 + b\omega^2 + c = 0$$

where a, b, and c are functions of the C_{ij}, S_i, and the elastic constants. The solutions are $\omega_i^2(k,\theta,\varphi)$ where i = 1, 2, 3. In the long wave limit $\omega_i = v_i k$, so that the cubic equation in ω^2 may be written as one in v^2, namely

(11) $$v^6 - Lv^4 + Mv^2 - N = 0$$

with solutions v_1^2, v_2^2, and v_3^2 which are functions of direction. In terms of the solutions of (11), the coefficients are given by

(12) $$L = v_1^2 + v_2^2 + v_3^2$$
$$M = v_1^2v_2^2 + v_2^2v_3^2 + v_3^2v_1^2$$
$$N = v_1^2v_2^2v_3^2 \ .$$

Now consider the required integral (2)

$$\int\left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right)d\Omega = \int\frac{(v_2v_3)^3 + (v_3v_1)^3 + (v_1v_2)^3}{(v_1v_2v_3)^3}\,d\Omega \, .$$

It can be rewritten as

(13) $$\int\frac{(v_2v_3)^3 + (v_3v_1)^3 + (v_1v_2)^3}{\left[(v_2v_3)^2 + (v_3v_1)^2 + (v_1v_2)^2\right]^{3/2}} \cdot \frac{\left[(v_2v_3)^2+(v_3v_1)^2 + (v_1v_2)^2\right]^{3/2}}{\left[(v_1^2v_2^2v_3^2)\right]^{3/2}}\,d\Omega$$
$$= \int R(M/N)^{3/2}d\Omega$$

where

(14) $$R = \frac{(v_2v_3)^3 + (v_3v_1)^3 + (v_1v_2)^3}{\left[(v_2v_3)^2 + (v_3v_1)^2 + (v_1v_2)^2\right]^{3/2}} \ .$$

It turns out that R is a very slowly-varying function of angle, (R must lie between 1 and $1/\sqrt{3}$). For example, for the worst case in a fcc metal, namely Pb, R lies between 0.62 and 0.76. Because of the small spread in R over the unit sphere, we expect it should be possible to obtain a good approximation to α_1 by writing it as

$$(15) \qquad \alpha_1 = (1/2\pi)^3 \bar{R} \int (M/N)^{3/2} d\Omega$$

where $\bar{R}$ is some appropriate average value of R over the unit sphere. The exact expression for $\bar{R}$ is of course given by

$$(16) \qquad \bar{R} = \frac{\int R(M/N)^{3/2} d\Omega}{\int (M/N)^{3/2} d\Omega} .$$

The numerator in the expression is just the integral we are trying to get. However, we now find an approximate value for $\bar{R}$ by expanding the integrands of both numerator and denominator in Kubic Harmonics, using only the first three terms. Thus

$$(17) \qquad \bar{R}_{\text{approx.}} = \frac{10R_A(M/N)_A^{3/2} + 16R_B(M/N)_B^{3/2} + 9R_C(M/N)_C^{3/2}}{10(M/N)_A^{3/2} + 16(M/N)_B^{3/2} + 9(M/N)_C^{3/2}}$$

$$= P/Q$$

Since R has a small spread over the unit sphere, P and Q vary in approximately the same way, and the errors in P and Q introduced by the approximation are about equal. Thus

$$(18) \qquad \bar{R} = \frac{P(1+\epsilon_1)}{Q(1+\epsilon_2)} \qquad\qquad (\epsilon_1 \sim \epsilon_2)$$

$$\approx \frac{P}{Q}(1+\epsilon_1)(1-\epsilon_2)$$

$$\approx \frac{P}{Q}(1+\epsilon_1-\epsilon_2)$$

Now P is nothing more than the Bhatia - Tauber (B - T) formula for α_1,

and ϵ_1 is the error introduced by that approximation; hence, provided that the integral in (15) can be accurately evaluated, we would expect this approximation to be considerably better than the three-term B - T approximation for α_1. The accuracy of this method may be extended even further by now using the six-term expansion for P and Q.

Evaluation of $\overline{R}$

The task of evaluating $\overline{R}$ is made quite simple if one first calculates the required velocities, then inserts them into the expression for $\overline{R}$, rather than expressing the numerator and denominator of $\overline{R}$ in terms of the elastic constants. The complexity of the expression derived on the basis of the latter approach is easily appreciated if one but looks at the general formulas for the velocities in terms of the elastic constants in the directions D, E, and F.

Data Used in the Calculations

The constants used in the calculations are given below. The sources of the data are included as well, and in the case of the elastic constants, the temperature at which they were measured. The metals are arranged in order of increasing anisotropy.

TABLE 1.

Metal	Density ρ		Elastic Constants					$N_0 = \frac{\text{Avogadro's No.}}{\text{At.Wt.}} \times \rho$	
	Value	Source	C_{11}	C_{12}	C_{44}	Temp.	Source	Value	Source of At. Wt.
W	19.0	HCP	50.1	19.8	15.1	RT	Kittel 14	6.222	HCP
Al	2.699	HCP	12.30	7.08	3.090	0°K	Sutton 15	6.030	HCP
Fe	7.88	HCP	23.7	14.1	11.6	RT	Kittel 14	8.502	HCP
Ag	10.492	HCP	12.0	8.97	4.37	291°K	Roehl 16	5.860	HCP
Cu	8.9326	HCP	17.0	12.3	7.52	RT	Kittel 14	8.470	HCP
Pb	11.34	HCP	4.8	4.1	1.4	RT	Kittel 14	3.297	HCP
K	0.87	HCP	0.46	0.37	0.26	RT	Kittel 14	1.341	HCP
Na	1.0066	HCP	0.970	0.830	0.580	0°K	Fuchs 17	2.6372	HCP

Remarks: The density is in gm/cc, the elastic constants are in units of 10^{11} dynes/cm^2, and N_0, the number of atoms/cc, is in units of 10^{22}/cc. HCP is the "Handbook of Chemistry and Physics, 35th Edition (1953-54)". RT stands for room temperature, and At. Wt. for atomic weight.

General Expressions for the Velocities of Long Waves

For long waves $ka/\sqrt{2}$ is very small, so that in the secular equation (I.28) we can replace

$\sin ka/\sqrt{2}$ by $ka/\sqrt{2}$

$\cos ka/\sqrt{2}$ by $1 - k^2a^2/4$.

Making these substitutions and writing v^2 for ω^2/k^2 in the solutions of (I.28), we obtain the velocities of long elastic waves in a cubic crystal.

(19a) Direction A (100)

$$\rho v_1^2 = c_{11}$$
$$\rho v_{t1}^2 = c_{44}$$
$$\rho v_{t2}^2 = c_{44}$$

(19b) Direction B (110)

$$\rho v_1^2 = c_{11} - \tfrac{1}{2}\epsilon$$
$$\rho v_{t1}^2 = c_{44}$$
$$\rho v_{t2}^2 = c_{44} + \tfrac{1}{2}\epsilon$$

(19c) Direction C (111)

$$\rho v_1^2 = c_{11} - (2/3)\epsilon$$
$$\rho v_{t1}^2 = c_{44} + (1/3)\epsilon$$
$$\rho v_{t2}^2 = c_{44} + (1/3)\epsilon$$

(19d) Direction D (210)

$$\rho v_1^2 = c_{11}/2 + c_{44}/2 + (\sqrt{9(c_{11} - c_{44})^2 + 16(c_{12} + c_{44})^2})/10$$
$$\rho v_{t1}^2 = c_{44}$$
$$\rho v_{t2}^2 = c_{11}/2 + c_{44}/2 - (\sqrt{9(c_{11} - c_{44})^2 + 16(c_{12} + c_{44})^2})/10$$

(19e) Direction E (211)

$$\rho v_1^2 = c_{44} + (5c_{11}+c_{12}-4c_{44})/12 + (\sqrt{(3c_{11}-c_{12}-4c_{44})^2+32(c_{12}+c_{44})^2})/12$$

$$\rho v_{t1}^2 = c_{44} + \epsilon/6$$

$$\rho v_{t2}^2 = c_{44} + (5c_{11}+c_{12}-4c_{44})/12 - (\sqrt{(3c_{11}-c_{12}-4c_{44})^2+32(c_{12}+c_{44})^2})/12$$

(19f) Direction F (221)

$$\rho v_1^2 = c_{44} + (5c_{11}+4c_{12}-c_{44})/18 + (\sqrt{(3c_{11}+4c_{12}+c_{44})^2+32(c_{12}+c_{44})^2})/18$$

$$\rho v_{t1}^2 = c_{44} + (5c_{11}+4c_{12}-c_{44})/18 - (\sqrt{(3c_{11}+4c_{12}+c_{44})^2+32(c_{12}+c_{44})^2})/18$$

$$\rho v_{t2}^2 = c_{44} + 4\epsilon/9$$

Velocities of Long Elastic Waves in Several Cubic Crystals

The velocities for W, Al, Fe, Ag, Cu, Pb, K, and Na, as calculated from (19) using the constants of Table 1 are: (in units of 10^5 cm/sec)

TABLE 2.

(a) Tungsten

Dir.	v_1	v_{t1}	v_{t2}
100	5.1350	2.8191	2.8191
110	5.1325	2.8191	2.8238
111	5.1316	2.8222	2.8222

(b) Aluminum

Dir.	v_1	v_{t1}	v_{t2}
100	6.7507	3.3837	3.3837
110	6.8812	3.3837	3.1097
111	6.9241	3.2036	3.2036

(c) Iron

Dir.	v_1	v_{t1}	v_{t2}
100	5.4842	3.8368	3.8368
110	6.2214	3.8368	2.4681
111	6.4484	2.9947	2.9947
210	6.0195	3.8368	2.9263
211	6.2651	3.4415	2.9020
221	6.3576	3.4710	2.6552

(d) Silver

Dir.	v_1	v_{t1}	v_{t2}
100	3.3820	2.0409	2.0409
110	3.7628	2.0409	1.2017
111	3.8814	1.5333	1.5333
210	3.6517	2.0409	1.5057
211	3.7810	1.8050	1.4877
221	3.8329	1.8249	1.3215

(e) Copper

Dir.	v_l	v_{t1}	v_{t2}
100	4.3625	2.9015	2.9015
110	4.9819	2.9015	1.6220
111	5.1719	2.1354	2.1354
210	4.8119	2.9015	2.0726
211	5.0180	2.5474	2.0492
221	5.0958	2.5744	1.8094

(f) Lead

Dir.	v_l	v_{t1}	v_{t2}
100	2.0574	1.1111	1.1111
110	2.2713	1.1111	0.55555
111	2.3383	0.78567	0.78567
210	2.2073	1.1111	0.77152
211	2.2804	0.96225	0.75872
221	2.3106	0.97554	0.64152

(g) Potassium

Dir.	v_l	v_{t1}	v_{t2}
100	2.2994	1.7287	1.7287
110	2.7854	1.7287	0.71919
111	2.9296	1.1580	1.1580
210	2.6675	1.7287	1.0772
211	2.8220	1.4713	1.0658
221	2.8742	1.4872	0.88985

(h) Sodium

Dir.	v_l	v_{t1}	v_{t2}
100	3.1043	2.4004	2.4004
110	3.8344	2.4004	0.83391
111	4.0487	1.5441	1.5441
210	3.6635	2.4004	1.4060
211	3.8923	2.0182	1.3919
221	3.9673	2.0402	1.1218

With the v_i calculated, it is now but a simple step to obtain $R(M/N)^{3/2}$, $(M/N^{3/2}$, and $\bar{R}_{\text{approx.}}$, since

$$R(M/N)^{3/2} = \sum_{i=1}^{3} (1/v_i^3)$$

$$(M/N)^{3/2} = \left[\sum_{i=1}^{3} (1/v_i^2)\right]^{3/2}$$

and $\bar{R}_{\text{approx.}}$ is given by (17) or by a six-term formula whose coefficients are those of (9). Nothing will be said now about the comparative values of the three- and six-direction values of $\bar{R}_{\text{approx.}}$. A full discussion on α_1 in a later section can be considered to be quite applicable to $\bar{R}_{\text{approx.}}$ since the error in the integral $\int (M/N)^{3/2}\, d\Omega$ can be made negligible in comparison with that of $\bar{R}_{\text{approx.}}$; therefore anything said about the accuracy of the Schiff approximation to α_1 will apply to $\bar{R}_{\text{approx.}}$, too.

TABLE 3.

(a) $R(M/N)^{3/2} \times 10^{15}$ $(cm/sec)^{-3}$

Dir. \ Metal	W	Al	Fe	Ag	Cu	Pb	K	Na
100	0.096655	0.054880	0.041472	0.26113	0.093922	1.5729	0.46938	0.17803
110	0.096442	0.062139	0.088371	0.71271	0.28337	6.6465	2.9280	1.8144
111	0.096376	0.063843	0.078199	0.57191	0.21262	4.2021	1.3277	0.55832
210				0.43112	0.16223	2.9996	1.0463	0.45240
211				0.49226	0.18462	3.4962	1.1844	0.50943
221				0.61563	0.23498	4.9458	1.7654	0.84215

(b) $(M/N)^{3/2} \times 10^{15}$ $(cm/sec)^{-3}$

Dir. \ Metal	W	Al	Fe	Ag	Cu	Pb	K	Na
100	0.15583	0.087195	0.069543	0.42764	0.15626	2.5292	0.79525	0.30275
110	0.15552	0.097529	0.13099	1.00493	0.39592	8.7428	3.7107	2.1767
111	0.15543	0.10020	0.12280	0.87822	0.32838	6.3328	2.0389	0.85359
210				0.65754	0.24802	4.4249	1.5460	0.65458
211				0.75442	0.28390	5.2207	1.7783	0.75299
221				0.91281	0.34811	7.0248	2.4880	1.1512

(c) $\bar{R}_{approx.}$

	W	Al	Fe	Ag	Cu	Pb	K	Na
3 Dir.	0.62015	0.63512	0.64993	0.67809	0.68063	0.71968	0.74108	0.78696
6 Dir.				0.66083	0.66015	0.68785	0.69251	0.71802

Determination of $\int (M/N)^{3/2}\, d\Omega$

The problem remaining is to determine the value of the integral $\int (M/N)^{3/2} d\Omega$, for which we require the coefficients of the cubic equation in v^2. These coefficients are obtained in terms of the elastic constants in Appendix A. The integral becomes

$$(20) \qquad \int (M/N)^{3/2}\, d\Omega = (\rho/c_{44})^{3/2} \int \left(\frac{p+tg}{r+sf+tg}\right)^{3/2} d\Omega$$

$$= (\rho/c_{44})^{3/2} \int I\, d\Omega$$

where $p = 3 + 2\,(\sigma + \xi)$

$r = \sigma + \xi + 1$

$s = \sigma^2\,(\sigma + 3\xi)\,/4$

$t = \sigma\,(\sigma + 2\xi)$

and

$$(21) \qquad \sigma = (c_{11} - c_{12} - 2c_{44})\,/c_{44}$$

$$\xi = (c_{12} + c_{44})\,/c_{44}\,.$$

f and g are functions of directions and are given by

$$(22) \qquad f = 4x^2y^2z^2$$

$$= \cos^2\theta \sin^4\theta \sin^2 2\varphi$$

$$g = x^2y^2 + y^2z^2 + z^2x^2$$

$$= \sin^2\theta - \sin^4\theta\,\left[1 - (\sin^2 2\varphi)/4\right]$$

x, y, and z are the directions cosines of the wave-vector $\underline{k}$ whose polar co-ordinates are θ, φ.

It is more convenient to write the integrand I in (20) as

$$(23) \qquad I = \left(\frac{a - g}{c + df - g}\right)^{3/2}$$

obtained by dividing numerator and denominator by $(-t)^{3/2}$. Thus

$$(24) \qquad a = -p/t = \frac{3 + 2\,(\sigma + \xi)}{-\sigma\,(\sigma + 3\xi)}$$

$$c = - r/t = \frac{\sigma + \xi + 1}{-\sigma(\sigma + 2\xi)}$$

$$d = - s/t = - \frac{1}{4}\sigma \frac{\sigma + 3}{\sigma + 2}$$

For all cubic metals $\sigma < 0$ and for elastic stability, it is necessary that $\sigma > -2$. In general σ decreases with increasing anisotropy and is zero for isotropic substances. For all cubic metals considered in this work, the integrand I is real and finite over the whole unit sphere.

We will now consider three methods of evaluating (20), each of which, through reasons of accurancy or amount of labour involved, is well-suited to only a portion of the σ interval.

Method I. Taylor Expansion About f and g.

We expand the integrand I in a Taylor series about f = 4/105 and g = 1/5, which are their average values over the unit sphere.

(25) $$I = [I] + \left[\frac{\partial I}{\partial f}\right](f - 4/105) + \left[\frac{\partial I}{\partial g}\right](g - 1/5) + \frac{1}{2!}\left\{\left[\frac{\partial^2 I}{\partial f^2}\right](f - 4/105)^2 + 2\left[\frac{\partial^2 I}{\partial f \partial g}\right](f - 4/105)(g - 1/5) + \left[\frac{\partial^2 I}{\partial g^2}\right](g - 1/5)^2\right\} + \ldots$$

where $[x]$ indicates 'x' taken for average values of f and g.

In those cases where the crystal is nearly isotropic (e.g., W and Al), terms in f may be regarded as negligible in comparison with those in g only, since d, the coefficient of f, decreases with increasing isotropy.

The Taylor series is integrated term by term over the surface of the unit sphere.

(26) $$(1/4\pi)\int I d\Omega = [I] + \left[\frac{\partial I}{\partial f}\right](1/4\pi)\int (f - 4/105) d\Omega + \left[\frac{\partial I}{\partial g}\right](1/4\pi)\int (g - 1/5) d\Omega + \ldots$$

Each term consists of

(a) an integral $(1/4\pi) \int (f - 4/105)^p \; (g - 1/5)^q \; d\Omega$,

and (b) $[x]$ whose value depends on the elastic constants of the material. The integral $(1/4\pi) \int (f - 4/105)^p \; (g - 1/5)^q \; d\Omega$ is tabulated below for values of p and q up to 5.

TABLE 4.

q \ p	0	1	2	3	4	5
0	1	0	1.7456×10^{-3}	7.5129×10^{-5}	8.7312×10^{-6}	7.0452×10^{-7}
1	0	2.7706×10^{-3}	8.9784×10^{-5}	1.2103×10^{-5}	8.9775×10^{-7}	
2	7.6190×10^{-3}	0.81191×10^{-5}	2.0523×10^{-5}	1.0229×10^{-6}		
3	-3.8362×10^{-4}	4.3750×10^{-5}	7.6677×10^{-7}			
4	1.3389×10^{-4}	-1.6608×10^{-6}				
5	-1.4062×10^{-5}					

We also require the values of $\left[\dfrac{\partial^n I}{\partial f^p \partial g^q}\right]$, taken at $f = 4/105$ and $g = 1/5$. General expressions for $(\partial^n I)/(\partial f^p \partial g^q)$ up to $n = 5$ $(p + q = n)$ will be found in Appendix B. These are applied to W, Al, Fe, and Pb; the results are tabulated below. Following the notation of the Appendix, we write

$$I = (P/Q)^{3/2}$$

$(\;\; {}^{n}I)/(\;\; f^{p} \;\;)$

where $P = a - g$

$Q = c + df - g$.

TABLE 5.

$$(\partial^{n}I)/(\partial f^{p}\partial g^{q})$$

(a) Tungsten

$P = -249.28$

$Q = -108.43$

$[I] = (P/Q)^{3/2} = 3.4857$

The other derivatives turn out to be negligible in comparison, and are therefore neglected. In the tables below, the maximum value of p or q is the same as the number of terms taken in the Taylor expansion.

(b) Aluminum

$P = 4.3989$ $Q = 1.8474$ $d = 0.11843$

p q	0	1	2	3
0	3.6744	-0.35331	0.056626	-0.012705
1	1.7304	-0.35765	0.087969	
2	2.1451	-0.59343		
3	3.8817			

(c) Iron

$P = 1.1313$ $Q = 0.35356$ $d = 0.49238$

p q	0	1	2	3	4	5
0	5.7237	-11.957	41.628	-202.91	1271.6	-9740.1
1	16.675	-68.690	356.91	-2313.6	18096	
2	110.66	-619.78	4176.9	-33447		
3	1061.0	-7474.7	61469			
4	13049	-111275				
5	201510					

(d) Lead

$P = 0.62397$ $Q = 0.18266$ $d = 0.60674$

q \ p	0	1	2	3	4	5
0	6.3137	-31.457	261.23	-3037.1	45,397	-829,380
1	36.669	-354.93	4377.6	-67520	1,257,800	
2	472.51	-6240.5	99,753	-1,899,000		
3	8788.9	-146,280	2,853,100			
4	210040	-4,231,800				
5	6,279,500					

All that now remains to obtain $(1/4\pi)\int I d\Omega$ is to combine the quantities of Tables 4 and 5 according to (26). For purposes of indicating the degree of convergence, the individual terms of the series are tabulated below.

TABLE 6.

Metal	Term 0	Term 1	Term 2	Term 3	Term 4	Term 5	Total
W	3.4857	0	0				3.4857
Al	3.6744	0	0.0072	-0.0002			3.6814
Fe	5.7237	0	0.2676	-0.0569	0.0355	-0.0142	5.9557
Pb	6.3137	0	1.0446	-0.4288	0.4973	-0.3804	7.0464

The number of terms required depends on the anisotropy of the crystal. Since the labour in calculating the terms is quite considerable, no attempts was made to go beyond five terms. It was found that five terms were sufficient to calculate the integral to better than 1% (in comparison with accurate results using elliptic integrals) when σ was greater than -1.

Method II. Taylor Expansion about $\sin^2 2\varphi = 1/2$

Consider the relative change in direction of a unit vector due to changes in θ and φ. It is obvious that over a large portion of the unit sphere, the direction does not change as much for a change in φ only as it does for one in θ only (this is especially evident for small θ). Consequently, the function of direction in the integrand will not vary in general as much with φ as with θ, so that an expansion of the integrand with respect to φ and a numerical integration with respect to θ should be an improvement over Method I, even when the number of terms in the expansion is small. Since the integrand is a function of φ through $\sin^2 2\varphi$, we expand about $\sin^2 2\varphi = 1/2$. The integrand, in terms of θ and φ, is

$$(28) \qquad I = \left[\frac{a - \sin^2\theta + \sin^4\theta\ (1 - (\sin^2 2\varphi)/4)}{c + d\cos^2\theta \sin^4\theta \sin^2 2\varphi - \sin^2\theta + \sin^4\theta\ (1 - (\sin^2 2\varphi)/4)}\right]^{3/2}$$

$$= \left[\frac{W + X\sin^2 2\varphi}{Y + Z\sin^2 2\varphi}\right]^{3/2}$$

where $W = a - \sin^2\theta + \sin^4\theta$

$X = -(\sin^4\theta)/4$

$Y = c - \sin^2\theta + \sin^4\theta$

$Z = \sin^4\theta\ (d\cos^2\theta - 1/4)$.

Thus,

$$(29) \qquad I = \left[I\right] + \left[\frac{\partial I}{\partial(\sin^2 2\varphi)}\right](\sin^2 2\varphi - 1/2)$$
$$+ \frac{1}{2}\left[\frac{\partial^2 I}{\partial(\sin^2 2\varphi)^2}\right](\sin^2 2\varphi - 1/2) + \ldots$$

with $\left[x\right]$ indicating that x is calculated at $\sin^2 2\varphi = 1/2$. Integrating

the separate terms with respect to φ and simplifying, we obtain

$$(30) \qquad (1/2\pi)\int_0^{2\pi} I d\varphi = \left(\frac{W + X/2}{Y + Z/2}\right)^{3/2} + \frac{3}{64}\,\frac{(XY - WZ)(XY - 5WZ - 2YZ)}{(W + X/2)^{1/2}(Y + Z/2)^{7/2}} + \ldots$$

The θ integration is performed numerically, taking intervals of $\cos\theta = 0.1$. The use of only the two terms in (30) is sufficient to give results accurate to within 1% for $\sigma > -1.5$. Except for σ values near 0, a region where Method I is best, this method appears to be the quickest of the three discussed here.

We apply this method to the calculation of $\int I d\Omega$ for Fe, Ag, Cu, and Pb. The quantities W, X, Y, and Z, calculated at intervals of $\cos\theta = 0.1$, appear in Appendix C. In Table 7, we combine them according to (30); finally, we obtain $(1/4\pi)\int I d\Omega$ by integrating numerically by Simpson's rule.

TABLE 7.

(a) Iron

$\cos\theta$	Term 1	Term 2	$(1/2\pi)\int_0^{2\pi} I d\varphi$	$(1/4\pi)\int I d\Omega$
0.0	5.0507	0.2711	5.3218	
0.1	5.0971	0.2568	5.3539	
0.2	5.2422	0.2159	5.4581	
0.3	5.5013	0.1556	5.6569	
0.4	5.8891	0.0876	5.9767	
0.5	6.3945	0.0298	6.4243	
0.6	6.9094	0.0007	6.9051	
0.7	7.1073	0.0004	7.1077	
0.8	6.5898	0.0029	6.5927	
0.9	5.3504	0.0004	5.3508	
1.0	3.9277	0.0000	3.9277	5.9563

(b) Silver

$\cos\theta$	Term 1	Term 2	$(1/2\pi)\int_0^{2\pi} I\,d\varphi$	$(1/4\pi)\int I\,d\Omega$
0.0	4.9614	0.4535	5.4149	
0.1	5.0158	0.4312	5.4470	
0.2	5.1889	0.3672	5.5561	
0.3	5.5099	0.2699	5.7798	
0.4	6.0230	0.1549	6.1779	
0.5	6.7491	0.0501	6.7992	
0.6	7.5560	-0.0025	7.5535	
0.7	7.9139	0.0064	7.9203	
0.8	7.1000	0.0103	7.1103	
0.9	5.3316	0.0010	5.3326	
1.0	3.6355	0.0000	3.6355	6.2321

(c) Copper

$\cos\theta$	Term 1	Term 2	$(1/2\pi)\int_0^{2\pi} I\,d\varphi$	$(1/4\pi)\int I\,d\Omega$
0.0	5.3253	0.5639	5.8892	
0.1	5.3841	0.5265	5.9106	
0.2	5.5733	0.4435	6.0168	
0.3	5.9281	0.3187	6.2468	
0.4	6.5039	0.1742	6.6781	
0.5	7.3353	0.0478	7.3831	
0.6	8.2897	-0.0055	8.2842	
0.7	8.7437	0.0180	8.7617	
0.8	7.8037	0.0186	7.8223	
0.9	5.7427	0.0016	5.7443	
1.0	3.8171	0.0000	3.8171	6.7832

(d) Lead

$\cos\theta$	Term 1	Term 2	$(1/2\pi)\int_0^{2\pi} I\,d\varphi$	$(1/4\pi)\int I\,d\Omega$
0.0	5.1445	0.8491	5.9936	
0.1	5.2101	0.8094	6.0195	
0.2	5.4247	0.6947	6.1194	
0.3	5.8468	0.5172	6.3640	
0.4	6.5834	0.2972	6.8806	
0.5	7.7633	0.0816	7.8449	
0.6	9.2956	-0.0123	9.2833	
0.7	10.1004	0.0697	10.1701	
0.8	8.5475	0.0531	8.6006	
0.9	5.6417	0.0032	5.6449	
1.0	3.4691	0.0000	3.4691	7.1801

Method III. Application of Elliptic Integrals to φ Integration

For $\sigma > -1.5$, we must, however, resort to the more accurate, as well as the most labourious method, wherein the φ integration is performed in terms of elliptic functions, followed by numerical integration with respect to θ. Let us write (28) as

$$I = (W/Y)^{3/2}\left(\frac{1 - n_1^2\sin^2 2\varphi}{1 - n_2^2\sin^2 2\varphi}\right)^{3/2} \tag{31}$$

where $n_1^2 = -X/W = \dfrac{\sin^4\theta}{4(a - \sin^2\theta + \sin^4\theta)}$

$$n_2^2 = -Z/Y = \frac{\sin^4\theta\,(1/4 - d\cos^2\theta)}{c - \sin^2\theta + \sin^4\theta}$$

Now consider the integral

$$(32) \qquad (W/Y)^{3/2} \int_0^{2\pi} \left(\frac{1 - n_1^2\sin^2 2\varphi}{1 - n_2^2\sin^2 2\varphi}\right)^{3/2} d\varphi$$

$$= \tfrac{1}{2}(W/Y)^{3/2} \int_0^{4\pi} \left(\frac{1 - n_1^2\sin^2\gamma}{1 - n_2^2\sin^2\gamma}\right)^{3/2} d\gamma$$

$$= 4(W/Y)^{3/2} \int_0^{\pi/2} \left(\frac{1 - n_1^2\sin^2\gamma}{1 - n_2^2\sin^2\gamma}\right)^{3/2} d\gamma$$

$$= 4(W/Y)^{3/2}\, J.$$

As the integration of J is dependent on the absolute and relative magnitudes of n_1^2 and n_2^2, it must be independently performed for the three regions

I. $n_2^2 < 0$

II. $1 > n_1^2 > n_2^2 > 0$

III. $1 > n_2^2 > n_1^2 > 0$

The integration is carried out in Appendix D, and only the results will be quoted here. The notation is that of Byrd and Friedman[18].

(33a) I. $n_2^2 < 0$

$$\int_0^{2\pi} I\,d\varphi = (W/Y)^{3/2} \left\{4k'E + 6n_1^2k'^3(E - k'^2K)/k^2 - 6n_1^2k'^3K\right\}$$

with $k^2 = 1 - k'^2 = |n_2^2|/(1 + |n_2^2|)$

(33b) II. $1 > n_1^2 > n_2^2 > 0$

$$\int_0^{2\pi} I\,d\varphi = (W/Y)^{3/2} \left\{ 4gE - \frac{4n_1^2}{n_2^2}\left[gE - \frac{\pi}{2}\frac{n_1}{n_2}\Lambda_0(\psi,k)\right]\right\}$$

with $k^2 = 1 - k'^2 = \dfrac{n_1^2 - n_2^2}{1 - n_2^2}$; $g^2 = 1/(1 - n_2^2)$; $\psi = \sin^{-1}\dfrac{n_2}{n_1}$

$$\Lambda_0(\psi,k) = (2/\pi)\left\{EF(\psi,k') + KE(\psi,k') - KF(\psi,k')\right\}$$

III. $1 > n_2^2 > n_1^2 > 0$

$$\int_0^{2\pi} I\,d\varphi = (W/Y)^{3/2}\left\{\frac{4k^2}{n_2^2 g}\left(\frac{E}{k'^2}+\frac{n_1^2 K}{n_2^2}\right)+\frac{2\pi n_1^3}{n_2^3}\Lambda_0(\psi,k)\right\}$$

with $k^2 = 1 - k'^2 = \dfrac{n_2^2 - n_1^2}{1 - n_1^2}$; $g^2 = 1/(1 - n_1^2)$; $\psi = \sin^{-1}\dfrac{n_1}{n_2}$

Tables of the functions K, E, and Λ_0, well-suited to the evaluation of these integrals, are available in an appendix in Ref. 18. Interpolation is, however, almost always necessary.

Method III is applied to the calculation of $\int I\,d\Omega$ for the fairly anisotropic metals Ag and Cu and the very anisotropic metals Pb, K, and Na. Most of the numerical work is tabulated in Appendix E; however, the quantities of interest, namely $(1/2\pi)\int_0^{2\pi} I\,d\varphi$ and $(1/4\pi)\int I\,d\Omega$ have been gathered in Table 8. In addition, the quantity $(1/2\pi)\int_0^{2\pi} I\,d\varphi$ is plotted against $\cos\theta$ for Ag, Pb, and Na in Fig. 1. The effect of anisotropy is very evident. We note especially the increasing contribution of the peak as we go from Ag to Na.

TABLE 8.

$\cos\theta$	$\frac{1}{2\pi}\int_0^{2\pi} I\,d\varphi$				
	Ag	Cu	Pb	K	Na
0.0	5.4945	5.9917	6.3038	8.7403	11.1353
0.1	5.5174	6.0089	6.2939	8.6319	10.7949
0.2	5.6051	6.0835	6.3094	8.4244	10.1100
0.3-	5.8052	6.2793	6.4598	8.3926	9.6889
0.4	6.1855	6.6874	6.9102	8.8563	10.0611
0.5	6.7997	7.3842	7.8460	10.1808	11.8388
0.6	7.5514	8.2835	9.2810	12.5325	15.7185
0.7	7.9113	8.7519	11.6428	14.4444	19.6127
0.8	7.1086	7.8204	8.5971	11.9334	15.0013
0.9	5.3323	5.7441	5.6449	7.2502	8.0127
1.0	3.6351	3.8169	3.4693	4.1084	4.1875
$\frac{1}{4\pi}\int I\,d\Omega$	6.2498	6.8077	7.2534	9.7313	11.897

Probable Error in Method III.

Since the criterion of accuracy for Methods I and II is Method III, it is necessary that we have some idea of the magnitude of possible errors in III. The sources of error in this method are two :

(1) the numerical θ integration, and

(2) the use of a two-term binomial expansion for $(1 - n_1^2 \sin^2\gamma)^{3/2}$ in region I. (see Appendix D).

It turns out for the metals considered that n_1^2 is quite small in this region, never exceeding 0.2 for the alkali metals and is less than 0.12 for fcc metals. (see Appendix E). When average values of n_1^2 and

Fig. 1.

$\int_0^{2\pi} I \, d\varphi$ by Method III for Ag, Pb, and Na.

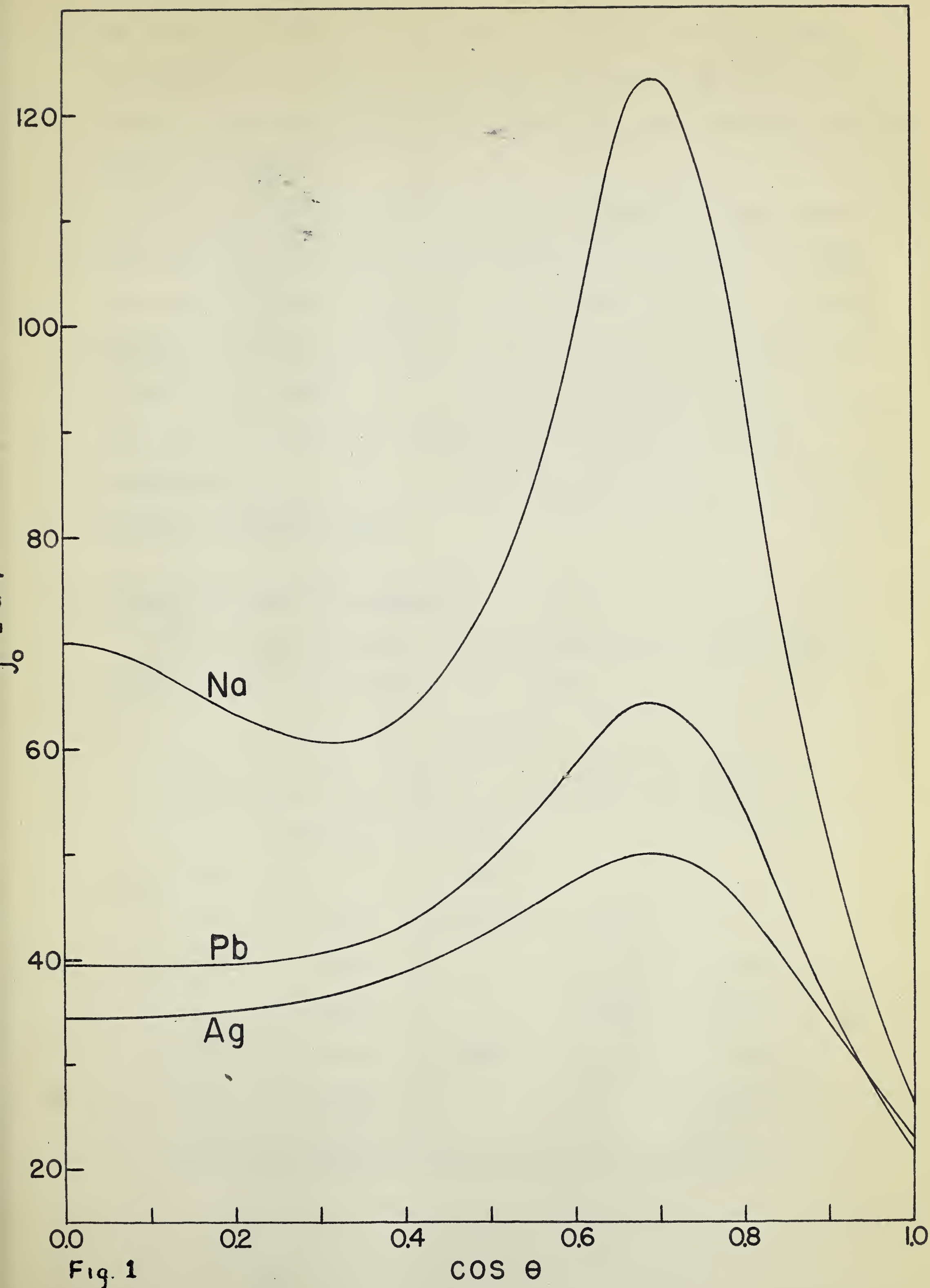

Fig. 1

$\sin^2\gamma$ are introduced, one finds that $1 - (3/2)n_1^2\sin^2\gamma$ differs from $(1 - n_1^2\sin^2\gamma)^{3/2}$ by about 1/10 of 1% for Na. The actual error, of course, is even less, since Region I represents about 1/3 of the whole range of integration.

The error introduced by the numerical integration, though greater than that due to the previous source, is still quite small. A rough check for sodium using integration intervals of 0.05 gave a result that differed by about 1/4 of 1% from that obtained using intervals of 0.1. It would appear safe to conclude that the accuracy of the method is about 1/3 of 1% for highly anisotropic metals and improves with increasing isotropy. It is certainly valid to use it as a measure of accuracy of Methods I and II.

$(1/4\pi)\int I d\Omega$ by the Three Methods

To facilitate comparison, we collect the results for $(1/4\pi)\int I d\Omega$ obtained from the three methods into a table.

TABLE 9.

Metal	σ	I	II	III
W	0.0066225	3.4857		
Al	-0.35714	3.6814		
Fe	-1.1724	5.9557	5.9563	
Ag	-1.3066		6.2321	6.2498
Cu	-1.3750		6.7832	6.8077
Pb	-1.5000	7.0464	7.1801	7.2534
K	-1.6538			9.7313
Na	-1.7586			11.897

From the table, and keeping in mind previous comments on the relative amount of labour involved in the application of these methods, it would appear that Method II, despite the fact that it is less accurate than III, is quite suitable for most purposes for σ values in the range -0.5 to -1.5. Above $\sigma = -0.5$, we find Method I to be sufficiently accurate as well as quickly applied. Below $\sigma = -1.5$, it is necessary to use Method III if the Debye θ accurate to 1% is desired.

Comparison of the Bhatia - Tauber and Schiff Approximations to α_1.

The data in Table 3(a) can be applied with little extra effort to the calculation of α_1 by the B - T method, since the $R(M/N)^{3/2}$ need only be added after multiplication by the appropriate coefficients. We will denote the various approximations as :

A.1 - three-term Bhatia - Tauber approximation, as given by (8) ;

A.2 - six-term Bhatia - Tauber approximation as given by (9) ;

A.3 - Schiff approximation using three-term $\overline{R}$. α_1 is given by

$$\alpha_1 = (1/2\pi^2)\overline{R}\,(1/4\pi)\int I d\Omega\,(\rho/c_{44})^{3/2} \;;$$

A.4 - Schiff approximation using six-term $\overline{R}$.

The results obtained from the four approximations are compiled in Table 10 on the next page.

TABLE 10. $\alpha_1 \times 10^{18}$

Metal	B - T Method		Schiff Approximation		
	A.1	A.2	A.3	A.4	$\frac{1}{4\pi}\int I d\Omega$ by
W	4.8880		4.8880		Method I
Al	3.0652		3.056		I
Fe	3.6656		3.470		II
Ag	27.736	24.452	25.257	24.614	III
Cu	10.692	9.2483	9.6093	9.3204	III
Pb	231.44	181.56	192.78	184.26	III
K	91.900	64.789	70.718	66.083	III
Na	51.870	30.446	34.292	31.286	III

From theoretical considerations, one would expect the Schiff approximations (A.3 and A.4) to lead to better results than those of Bhatia - Tauber (A.1 and A.2), and this seems to be confirmed by computations for actual cases. It can be seen that calculations using A.4 do not differ substantially from those of A.3, indicating that A.3 is already very good. Therefore, one expects that A.4 leads to very nearly the correct results. This is not the behaviour, however, of the Bhatia - Tauber approximation, where the great improvement of A.2 over A.1 suggests that A.2 itself could be improved, perhaps considerably, by using more than six terms in the B - T formula. A comparison of α_1's as calculated by A.2 and A.4 does indicate that A.2 is indeed quite good ; in fact, it is within 3% (1% in Θ_D) of A.4 for all σ values down to -1.75 and this region contains perhaps nearly all of the cubic metals. A point in favour of A.2 is that it

involves only one-third to one-half of the calculations required in A.4.

The accuracy of A.4 depends strictly on that of $\bar{R}$, since $\int I d\Omega$ can be obtained almost as exactly as required. Without calculating the influence of higher Kubic Harmonics on $\bar{R}$, it is not possible to state definitely how good $\bar{R}$ is, but considering that A.4 represents an improvement over A.3 of 10% for the worst case (Na), it is probable that A.4 leads to results for α_1 that are not out by more than a couple of percent. Thus θ_D by A.4 is probably better than 1% in the case of Na, with even better results, of course, for more isotropic metals.

Results for θ_D

Finally, using the best values of $\int I d\Omega$ and $\bar{R}$, the following results for θ_D have been obtained.

TABLE 11

Metal	$\bar{R}$	$(1/4\pi) \int I d\Omega$	θ_D °K		
			This Work	Blackman[19]	Quimby[8]
W	0.62015	3.4857	371		
Al	0.63512	3.6814	429		
Fe	0.64993	5.9563	462	461	
Ag	0.66083	6.2498	212	212	211.3
Cu	0.66015	6.8077	332		
Pb	0.68785	7.2534	89.5		
K	0.69251	9.7313	93.4		
Na	0.71802	11.897	150	143	

Comparisons between these results and any experimental values that might be available are, with two exceptions, not valid, since the elastic constants data used here were obtained at room temperature. In addition, the use of different constants makes it useless to quote the results of other theoretical calculations available in the literature. However, in the case of Fe, Ag, and Na, comparisons with values found in Blackman[19] are possible, since the elastic constants used there are the same (or very nearly so), as those of this work. In addition, Θ_D for silver calculated on the basis of the Quimby - Sutton approximation is available for comparison.

Accuracy of Calculations

On the basis of the approximations used, the accuracy of the results for Θ_D is estimated to be better than 1%. It is not likely that the numerical work would introduce any significant errors, since the calculations were almost always carried out using five figures. It is to be understood, however, that only three of these, at most, are significant, as the experimental data used are not usually known any better than that. It would seem safe to conclude then, that the Schiff approximation A.4 is at least as good as any of the data that one would generally have to use.

PART III. DEBYE CHARACTERISTIC TEMPERATURE OF SILVER

General Expression for the Specific Heat

The specific heat, c_v, per atom at constant volume is given by (I.10) as

$$(1) \qquad N_o V c_v = VK(\hbar/KT)^2 \int G(\omega)\omega^2 e^{\hbar\omega/KT}(e^{\hbar\omega/KT} - 1)^{-2} d\omega$$

where

$$(2) \qquad VG(\omega)d\omega = \frac{V}{(2\pi)^3} d\omega \int \sum_{i=1}^{3} k^2(\omega_i,\theta,\varphi) \frac{dk(\omega_i,\theta,\varphi)}{d\omega_i} d\Omega$$

Approximations to G(ω)

For the determination of $G(\omega)$ we require the complete dispersion relations between ω and k. It is clear that what has been said in Part II with regard to the complexity of these relations in the long wavelength limit and to the difficulty of carrying out the necessary integration obtains here à fortiore. We thus again resort to approximate methods. The two methods used here are (1) the three-term Houston approximation, and (2) and alternative three-term formula whose coefficients are determined by the requirements that

(a) $G(\omega)$ give the correct number of modes, and

(b) θ_D at $T = 0^oK$ agree with the experimental value.

Houston Approximation

We have already encountered the Houston approximation in Part II, so that it is sufficient here to merely write down the expression for $G(\omega)$ obtained from it.

$$(3) \qquad G(\omega) = \frac{F}{(2\pi)^3} \frac{4\pi}{35} \sum_{i=1}^{3} \left\{10(k^2dk/d\omega_i)_A + 16(k^2dk/d\omega_i)_B + 9(k^2dk/d\omega_i)_C\right\}$$

The factor F is introduced to ensure that

(4) $$\int G(\omega)\,d\omega = 3N_o.$$

Determination of F

If we denote the maximum value of k along the directions A, B, and C by $k_A(m)$, $k_B(m)$, and $k_C(m)$, respectively, then

(5) $$\begin{aligned}\int G(\omega)\,d\omega &= \frac{F}{(2\pi)^3}\frac{4\pi}{35}\left\{10k_A^3(m) + 16k_B^3(m) + 9k_C^3(m)\right\}\\ &= 3N_o\end{aligned}$$

The k-vectors are confined to the first Brillouin zone, since solutions for k outside this zone give no new modes of vibration. Therefore the k(m) are to be determined by finding the point of intersection of the k-vector with the boundary of the first Brillouin zone. For fcc crystals, the first Brillouin zone is marked out by the (200) and (111) planes and the k(m) are[20]

(6) $$\begin{aligned}k_A(m) &= 2(\pi/a)\\ k_B(m) &= \tfrac{3}{2}(\pi/a)\\ k_C(m) &= \sqrt{\tfrac{3}{2}}(\pi/a)\end{aligned}$$

Equations (5) and (6) give for F:

(7) $$F = 0.95664.$$

Physical Basis of F

Physically, F arises from the deviations of the Brillouin zone from spherical symmetry. For small k, whose contributions are significant at low temperatures, the shape of the Brillouin zone is clearly of no importance. Thus, no F factor is required in this case,. As the temperature rises, ever larger k values contribute to the specific

heat, until k values of the magnitude of k(m) are significant. However, these k(m) are not of equal length in every direction, and the resulting asymmetry plus the use of a finite number of directions in Houston's approximation result in a necessity for an adjusting factor F. The F that is used in the calculations is an average value, since no factor is required for small k, and some factor larger than F is required in the region beyond the Brillouin surface closest to the origin. Thus, the introduction of this factor into $G(\omega)$ cannot in general lead to the right results for c_v at low temperatures. However, in the case of silver, the θ_D at 0°K obtained by this method (i.e. the B - T formula) is in agreement with the latest experimental value.[21] This is certainly due to a number of compensating factors: (1) the use of a three-term approximate formula, (2) the use of approximate values for the elastic constants at 0°K, and (3) the possibility that the experimental results are not exact.

Adjusted Constants Method

In the second method of calculating the frequency spectrum, the Houston coefficients 10, 16, and 9 are replaced by 10, a, and b, and [illegible] a and b are then determined by requiring that

$$\int G(\omega)\,d\omega = 3N_o, \text{ and} \tag{8}$$

$$\frac{1}{(2\pi)^3}\;\frac{4\pi}{10+a+b}\sum_{i=1}^{3}\left\{10\,(k^2dk/d\omega_i)_A + a(k^2dk/d\omega_i)_B + b(k^2dk/d\omega_i)_C\right\} = \alpha_1 \tag{8a}$$

where α_1 is the value obtained by A.4 (Part II). These two conditions automatically ensure that θ_D is correct at the two extremes of low and high temperatures. Good results at the high temperature end are assured because $\int G(\omega)E(x)\,d\omega$ is nearly independent of the shape of the $G(\omega)$ curve,

since E(x) changes very slowly with ω when T is large ($x = \hbar\omega/KT$). What we nearly have is a constant x $\int G(\omega)d\omega$ and $\int G(\omega)d\omega$ has already been fixed by the first condition. At the low temperature end, agreement is obtained through α_1. This method will hereafter be referred to as the "Adjusted Constants Method" (AC Method).

Determination of a and b

Because it is the most accurate value of α_1 that we have, we will use the one obtained from A.4 (Part II) for determining a and b. However, before inserting it in (8a), we must first convert it to the 0°K value, since it was calculated using room temperature elastic constants, the only temperature at which the elastic constants for silver have been measured. In a later section our approximate extrapolation of the room temperature values of the elastic constants to 0°K is equivalent to multiplying α_1 by $(1.183)^{-3/2} = 0.7772$ to convert it to the 0°K value to give

(9) $\alpha_1 = 19.150 \times 10^{-18}$ (cm/sec)$^{-3}$ (0°K)

Then, from (8) we obtain (using $N_o = 5.9 \times 10^{22}$/cc),

(10) $a = 7.2083$

$b = 7.1006$

and the approximate expression for the frequency spectrum becomes

$$G(\omega) = \frac{1}{(2\pi)^3}\,\frac{4\pi}{24.309}\sum_{i=1}^{3}\Big\{10(k^2dk/d\omega_i)_A + 7.2083(k^2dk/d\omega_i)_B + 7.1006(k^2dk/d\omega_i)_C\Big\} \tag{11}$$

In comparing (11) with the Houston approximation (3), we note that the contribution from the B direction has been considerably decreased

while the contributions from the A and C (especially A) directions have been increased.

Dispersion Relations

In order to obtain $G(\omega)$ by either of the approximations (3) or (11) we require the solutions of the secular equation (1.28) along the three principal directions of the crystal, A, B, and C. They are:

(12a) Direction A (100)

$$\omega_l^2 = (8c_{11}/a^2\rho)\sin^2(ak/2\sqrt{2})$$
$$\omega_{t1}^2 = (8c_{44}/a^2\rho)\sin^2(ak/2\sqrt{2})$$
$$\omega_{t2}^2 = (8c_{44}/a^2\rho)\sin^2(ak/2\sqrt{2})$$

(12b) Direction B (110)

$$\omega_l^2 = (8/a^2\rho)\sin^2(ak/4)\left\{2c_{11} - \epsilon - (2c_{11} - c_{44} - \epsilon)\sin^2(ak/4)\right\}$$
$$\omega_l^2 = (8/a^2\rho)\sin^2(ak/4)\left\{2c_{44} - (2c_{44} - c_{11})\sin^2(ak/4)\right\}$$
$$\omega_{t2}^2 = (8/a^2\rho)\sin^2(ak/4)\left\{2c_{44} + \epsilon - (c_{44} + \epsilon)\sin^2(ak/4)\right\}$$

(12c) Direction C (111)

$$\omega_l^2 = (2/a^2\rho)(3c_{11} - 2\epsilon)\sin^2(ak/\sqrt{6})$$
$$\omega_{t1}^2 = (2/a^2\rho)(3c_{44} + \epsilon)\sin^2(ak/\sqrt{6})$$
$$\omega_{t2}^2 = (2/a^2\rho)(3c_{44} + \epsilon)\sin^2(ak/\sqrt{6})$$

Temperature Dependence of $G(\omega)$

Because of the dependence of the elastic constants on temperature, it is obvious that $G(\omega)$ will vary with temperature. Thus, strictly speaking, in calculating c_v at any temperature, the $G(\omega)$ appropriate to that temperature should be used. It can be appreciated that the labour involved in carrying out a complete calculation of the Debye temperature over the whole temperature

range, taking into account the detailed variation of the elastic constants, is quite substantial. However, for the case of silver, some simplifying assumptions can, of necessity, be made, although it is known that they are not strictly true. They are:

(1) that the elastic constants vary linearly with temperature, and

(2) that the temperature coefficient of the constants is the same for all of them.

Adjustment of $G(\omega)$ for Temperature Variation

Assuming, then, that the three elastic constants vary with temperature in precisely the same way, it is clear from (12) that all the dispersion relations can be written in the form

$$(13) \quad \omega = c_{44}^{1/2} f(k)$$

and that the temperature dependence of ω is contained solely in the factor $c_{44}^{1/2}$ (for convenience, we will leave out the subscript 44 in what follows). Let $x = \omega/c^{1/2}$; then we can write

$$(14) \quad k^2 \frac{dk}{d\omega} = k^2 \frac{dk}{dx} \frac{dx}{d\omega}$$

$$= c^{-1/2} k^2 \frac{dk}{dx}$$

where $k^2 \frac{dk}{dx}$ is some function of x. Thus

$$(15) \quad G(x) = c^{-1/2} g(x)$$

where $g(x)$ involves a summation of the $k^2 \frac{dk}{dx}$ terms. Denoting c_{44} at 0°K and at any other temperature T by c_o and c_T respectively, we have for a given x

$$(16) \quad g(x) = c_o^{1/2} G_o(x) = c_T^{1/2} G_T(x)$$

Hence

$$(17) \quad G_T(x) = (c_o/c_T)^{1/2} G_o(x)$$

and

(18) $$G_T(\omega) = (c_o/c_T)^{1/2}\, G_o\left[(c_o/c_T)^{1/2}\omega\right]$$

Thus, once the frequency spectrum is known at 0°K, it can easily be determined at any other temperature.

Choice of Elastic Constants for 0°K

As previously mentioned, measured values of the elastic constants for silver are known at present only for room temperature. Thus, to determine the 0°K values, it is necessary to carry out some reasonable extrapolation procedure. Since the results obtained here are to be compared to those of Bhatia and Horton[2], their procedure is employed here, too. The room temperature values

(19) $$\left.\begin{aligned} c_{11} &= 12.0 \\ c_{12} &= 8.97 \\ c_{44} &= 4.37 \end{aligned}\right\} \times 10^{11}\ \text{dynes/cm}^2 \qquad (T = 291^\circ K)$$

were converted to 0°K values by multiplying the constants by the factor 1.183, giving

(20) $$\left.\begin{aligned} c_{11} &= 14.19 \\ c_{12} &= 10.62 \\ c_{44} &= 5.17 \end{aligned}\right\} \times 10^{11}\ \text{dynes/cm}^2 \qquad (T = 0^\circ K)$$

If we calculate α_1 by A.4 (Part II) using the elastic constants as given by (20), we obtain (see eq. 9)

$$\alpha_1 = 19.150 \times 10^{-18}\ (\text{cm/sec})^{-3}\ .$$

Now this value of α_1 leads to a result for Θ_o at 0°K that is about 6° higher than the latest experimental value[21] . Since A.4 is known to be

very nearly exact, we conclude that our extrapolation procedure for the elastic constants is probably not good enough. In an approximate attempt to correct this discrepancy between the theoretical and experimental values of Θ_D, we will use an extrapolation factor 1.123 instead of 1.183. Although it may first appear that this would require a recalculation of the coefficients in our approximation (11) for $G(\omega)$, it can clearly be incorporated in (18). The elastic constants determined on the basis of the extrapolation factor 1.123 are

$$(21) \qquad \left.\begin{aligned} c_{11} &= 13.48 \\ c_{12} &= 10.07 \\ c_{44} &= 4.906 \end{aligned}\right\} \times 10^{11} \text{ dynes/cm}^2. \qquad (T = 0\ ^{\circ}K)$$

Other Constants Used in Calculations

The other constants needed to calculate $G(\omega)$ are N_o, the number of atoms per unit volume, and ρ, the density of the substance. These are taken to be, as in Ref. 2,

$$(22) \qquad N_o = \sqrt{2}/a^3 = 5.9 \times 10^{22}/\text{cc} \ ; \ \rho = 10.5 \text{ gm/cc}.$$

N_o and ρ also vary with temperature, but this variation is small and is neglected.

Procedure Used in the Calculation of G( )

In calculating $G(\omega)$, rather than solving for k and $dk/d\omega$ for chosen values of ω, which, at least in the case of Direction B would be very difficult, the reverse procedure is used, whereby the and $d\omega/dk$ are calculated for suitably spaced values of k. A $k^2 dk/d\omega$ vs. $(a^2\rho)^{1/2}$ curve is then plotted for each solution of the secular equation (seven different solutions in all among the three directions). Finally, the ordinates corresponding to $(a^2\rho)^{1/2}$ values suitably chosen for purposes of numerical integration

are combined according to the Houston (3) or AC (11) formula to give $G(\omega)$. For small values of ω, it is desirable instead to use the analytic expression for $G(\omega)$, namely

$$(23) \qquad G(\omega) = \alpha_1 \omega^2 = C\omega^2 a^2$$

since this region contributes significantly to c_v at low temperatures and the graphical results may be somewhat unreliable here. Using $0^\circ K$ elastic constants (20) we find that for silver

$$(24a) \qquad G(\omega) = 2.4722 \times 10^{-3} \quad \rho a^2 \omega^2$$

on the basis of the Bhatia-Tauber formula including F and

$$(24b) \qquad G(\omega) = 2.1938 \times 10^{-3} \quad \rho a^2 \omega^2$$

on the basis of A.4 (Part II).

These formulas were found to be valid to 1% for $\omega(a^2\rho)^{1/2}$ up to about 2×10^5.

Treatment of Singularities in G(ω)

Because $d\omega/dk$ becomes zero when $k = k(m)$ (except for the two transverse solutions in Direction B), the frequency distribution function as determined by either of the two methods has several infinities. However, the area under the curve at these singularities is always finite, and for purposes of numerical integration, the singularities can be replaced by finite peaks of equal area.

Comparison of G(ω) Obtained from the Two Approximations

In Fig. 2, we compare the $G(\omega)$ calculated from (3) and (11). The solid curve represents $G(\omega)$ as obtained from Houston's approximation (3), while the dotted curve represents that obtained from the AC approximation (11).

Fig. 2.

Frequency Spectrum of Silver

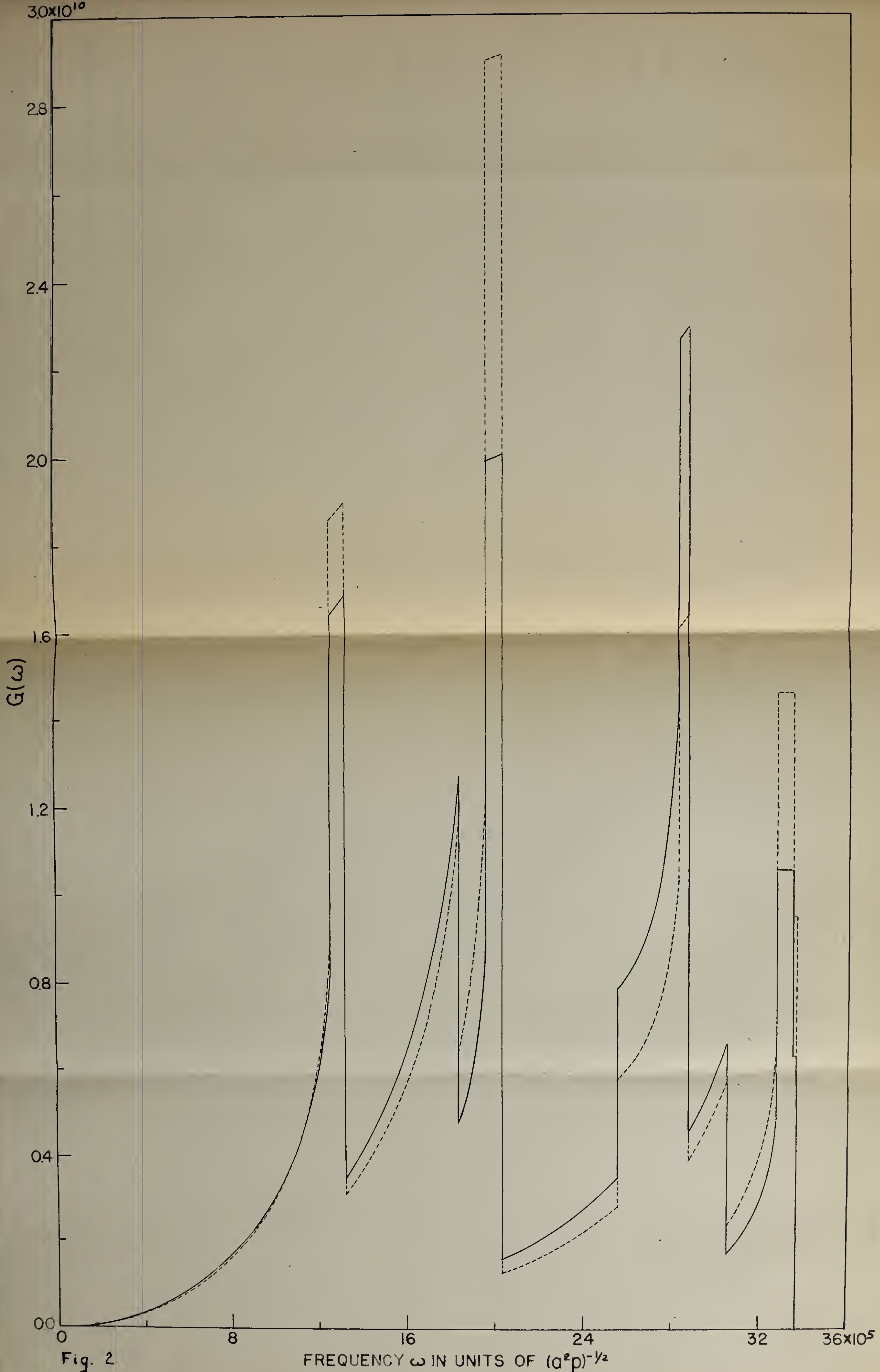
3.0×10¹⁰
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
G(ω)
0
8
16
24
32
36×10⁵
FREQUENCY ω IN UNITS OF (a²p)^-½

Fig. 2

We draw attention to the changes in the relative heights of the of the peaks. As expected, those peaks due to Direction A $\left[\omega(a^2\rho)^{1/2} \times 10^{-5} = 19.6 - 20.337 \text{ and } 32.75 - 33.7\right]$ and Direction C $\left[\omega(a^2\rho)^{1/2} \times 10^{-5} = 12.5 - 13.2 \text{ and } 32.75 - 33.5\right]$ have been enhanced by the AC method, while those from Direction B $\left[\omega(a^2\rho)^{1/2} \times 10^{-5} = 18.352,\ 28.293 - 28.75, \text{ and } 30.5\right]$ have been depressed. The increase in the contributions to $G(\omega)$ from Directions A and C has an appreciable effect on Θ_D in the temperature region above $T = 15^\circ$K, but this will be discussed more fully in a succeeding section.

Debye Temperature of Silver

The specific heat c_v per atom at constant volume can now be calculated at several temperatures from (1) using numerical integration. Instead of comparing experimental and calculated values of c_v, we compare the corresponding Debye temperatures Θ_D, readily obtained from c_v. A table of Θ_D/T vs. $c_v/3K$ is available in Ref. 22. The results are plotted in Fig. 3. Curves (a), (b), and (c) are the results of the present calculations,

(a) using 0°K elastic constants (15) and Houston's approximation to $G(\omega)$;

(b) using Houston's approximation to $G(\omega)$, adjusted for the temperature variation of the elastic constants by (13) with

$$(25) \qquad c_0/c_T = 5.17 \times 10^{11}/c_T, \text{ and}$$

$$c_T = (5.17 - 0.0026667T) \times 10^{11} \text{ dynes/cm}^2 ;$$

(c) using the AC approximation to $G(\omega)$, adjusted for the temperature variation of the elastic constants by (18) with

Fig. 3.

Debye Characteristic Temperature of Silver from 0° - 150°K.

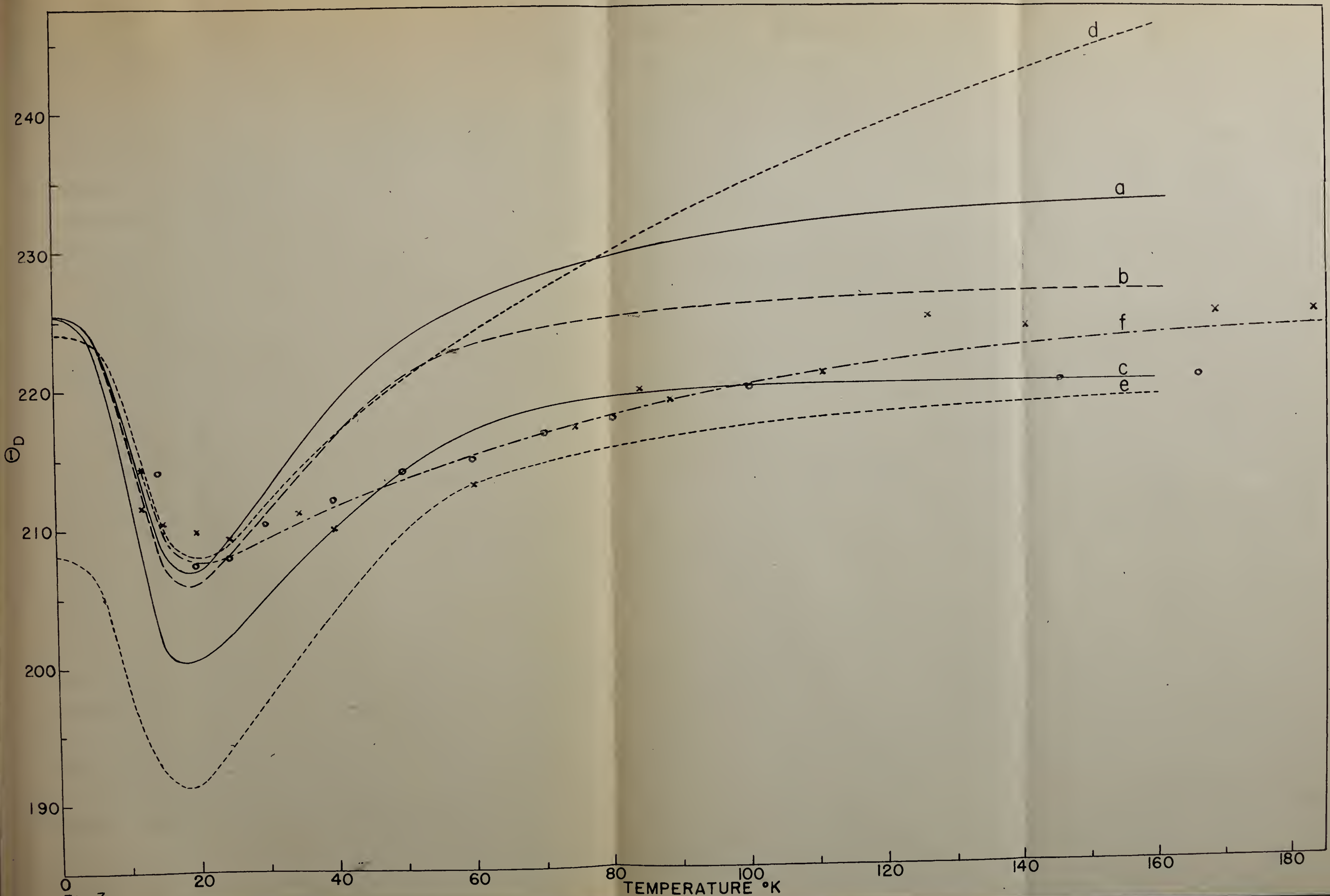
d
a
b
f
c
e
240
230
220
210
200
190
Θ_D
0
20
40
60
80
100
120
140
160
180
TEMPERATURE °K

Fig. 3.

$$(26)\qquad c_0/c_T = 5.17 \times 10^{11}/c_T, \text{ and}$$

$$c_T = (4.906 - 0.001787\ T) \times 10^{11}\ \text{dynes/cm}^2.$$

Curve (f) represents a smoothening out of the experimental results. Points marked 'x' are due to Eucken, Clusius, and Woitinek[23] and those marked 'o' are due to Meads, Forsythe, and Giauque[24]. In addition, the calculated results obtained by Bhatia and Horton[2] are included as curves (d) and (e). Both were obtained by using Houston's approximation to $G(\omega)$ and

(d) 0°K elastic constants (20) and,

(e) room temperature constants (19).

Theory and Experiment Below 15°K

Although available, no experimental results have been shown for the temperature region below 15 °K. The work of Keesom and Kok[25] gives a sharp maximum in the θ_D - T curve around 5° followed by a minimum around 3°. These findings are corroborated, within experimental error, by the results of Keesom and Pearlman[26]. However, these two groups of results are at variance with those of Corak et al.[21] which indicate that the atomic heat obeys the T^3 law up to at least 4 °K; consequently, θ_D is constant at 225.3° to 4 °K. In the case of Corak, it must be noted that only after an adjustment of the 1948 helium vapour pressure - temperature scale did the T^3 law adequately represent the experimental results. However, essentially the same adjustments were indicated by the work, along quite different lines, of other investigators. Thus, Corak's corrections would appear to be justified.

A small part of the discrepancy between theory and Corak's results may have its origin in the numerical integration. The value of θ_D

obtained by numerical integration of (1) is quite sensitive to the frequency interval taken. This was found to be especially so for 2 $^{\circ}$K, where a wide discrepancy between θ_0 and θ_2 was traced to this source; by taking smaller integration intervals, an improvement substantial enough to give agreement between these two values was obtained.

Theory and Experiment Above 15°

A feature common to all the theoretical curves is the presence of a deep minimum around 20 $^{\circ}$K. This minimum is primarily due to the first peak in the $G(\omega)$ curve, although there is some contribution from the peak occurring around $\omega(a^2\rho)^{1/2} = 20 \times 10^5$. Thus, because both of these peaks have been enhanced by the AC Method, the minimum in curve (c) has been considerably deepened. On the other hand, it is largely because of the second peak that we obtain such good agreement near 60 $^{\circ}$K for curve (c). The results indicate that what is required is a redistribution in the $G(\omega)$ curve, with the first two or three peaks somewhat reduced and the contribution of the portion beyond $\omega(a^2\rho)^{1/2} = 20 \times 10^5$ increased.

Since the peaks have their origin in the approximations through the choice of directions used, it is quite likely that the actual $G(\omega)$ is flatter than that which has been used here. This is confirmed by the $G(\omega)$ for aluminum, obtained using thousands of directions[27]. There are two maxima, a fairly smooth one corresponding to the transverse vibrations, and a sharper one from the longitudinal vibrations.

Some of the discrepancy between theory and experiment probably has its origin in the elastic constants and their variation with temperature.

The limitations of the procedure used to adjust $G(\omega)$ for this variation are evident from the assumptions made about the behaviour of the constants with temperature. An error of a couple of percent from this source alone is quite conceivable.

Another factor is the possible influence of anharmonic terms, whose effect would naturally be most evident at higher temperatures. We note that curve (b) (for which $G(\omega)$ was temperature adjusted) does not remove all the discrepancy between theory (curve a) and experiment at the high temperature end, so that one might suspect the contribution of anharmonic terms to the specific heat. However, since the temperature correction itself is somewhat uncertain, we should not jump to any conclusions regarding the effect of anharmonicity.

Conclusions

Taken over the whole temperature range, the Debye characteristic temperatures calculated on the basis of the Bhatia theory (curve d) and those on the basis of the Born and Begbie theory (curve a), using the Houston approximation to $G(\omega)$ in both of them, appear to be about equivalent. The former theory leads to slightly better results at the minimum around 20°, but beyond about 80°, the latter theory fits the experimental results more closely, but the differences are really quite small.

The results do seem to indicate, however, that a three-term approximation to $G(\omega)$ is not likely to lead to results for θ_D that are correct over the whole temperature range. The number of directions in such approximations is too small to give adequately the frequency

distribution. It would seem likely then that calculations using a larger number of terms in $G(\omega)$ may lead to a $G(\omega)$ more representative of the actual picture, and thus to better results for the specific heats. Such a calculation might indicate significant differences in the specific heats as obtained from the Bhatia and the Born and Begbie theories.

Accuracy of Work

It is estimated that the numerical work is at least good to 1%. Calculations were always carried out to five figures, while all graph readings were good to three figures. Intervals for any numerical integration were always sufficiently close-spaced to capture all the details of the variations of the integrand.

APPENDIX A. Determination of Coefficients of Cubic Equation in v^2.

Let x, y, z be the direction cosines of the wave-vector k.

$$k_1 = xk; \qquad k_2 = yk; \qquad k_3 = zk$$

In the long wave limit (ka → 0), we can replace cosines and sines of ka by their Taylor expansions of one or two terms. Thus the C_{ij} and S_i of the secular equation (I.28) become

$$(1) \qquad \begin{aligned} C_{12} &= 1 - (a^2k^2/4)(x^2 + y^2) \\ C_{23} &= 1 - (a^2k^2/4)(y^2 + z^2) \\ C_{31} &= 1 - (a^2k^2/4)(z^2 + x^2) \end{aligned}$$

$$S_1 = xak/\sqrt{2}; \qquad S_2 = yak/\sqrt{2}; \qquad S_3 = zak/\sqrt{2}$$

Substituting these expressions into the D_{ij} , we obtain

$$(2) \qquad \begin{aligned} D_{11} &= (k^2/\rho)\left\{\alpha(1 - x^2) + \beta(1 + x^2)\right\} \\ &= (k^2/\rho)\left\{c_{44} + x^2(c_{11} - c_{44})\right\} \\ &= (k^2/\rho)c_{44}\left\{1 + x^2(\sigma + \xi)\right\} \\ D_{22} &= (k^2/\rho)c_{44}\left\{1 + y^2(\sigma + \xi)\right\} \\ D_{33} &= (k^2/\rho)c_{44}\left\{1 + z^2(\sigma + \xi)\right. \\ D_{12} = D_{21} &= (k^2/\rho)xy\xi c_{44} \\ D_{23} = D_{32} &= (k^2/\rho)yz\xi c_{44} \\ D_{31} = D_{13} &= (k^2/\rho)zx\xi c_{44} \end{aligned}$$

where $\sigma = (c_{11} - c_{12} - 2c_{44})/c_{44}$

$$\xi = (c_{12} + c_{44})/c_{44}$$

From

$$(3) \qquad \begin{vmatrix} D_{11} - \omega^2 & D_{12} & D_{13} \\ D_{12} & D_{22} - \omega^2 & D_{23} \\ D_{13} & D_{23} & D_{33} - \omega^2 \end{vmatrix} = 0$$

we obtain the cubic equation in ω^2

$$(4)\qquad \omega^6 - \omega^4(D_{11} + D_{22} + D_{33}) + \omega^2(D_{11}D_{22} + D_{22}D_{33} + D_{33}D_{11} - D_{12}^2 - D_{23}^2 - D_{31}^2)$$
$$- (D_{11}D_{22}D_{33} + 2D_{12}D_{23}D_{31} - D_{12}^2D_{33} - D_{23}^2D_{11} - D_{31}^2D_{22}) = 0$$

Next, we substitute for the D_{ij} their expressions in terms of the elastic constants, replace ω^2/k^2 by v^2, and

$x^2y^2 + y^2z^2 + z^2x^2$ by g

$4x^2y^2z^2$ by f

We obtain

$$(5)\qquad v^6 - (v^4/\rho)(c_{11} + 2c_{44}) + (vc_{44}/\rho)^2\{3 + 2(\sigma + \xi) + g(\sigma + 2\xi)\}$$
$$- (c_{44}/\rho)^3\{1 + \sigma + \xi + (f\sigma^2/4)(\sigma + 3\xi) + g(\sigma + 2\xi)\} = 0$$

which we write as

$$(6)\qquad v^6 - (v^4/\rho)(c_{11} + 2c_{44}) + (vc_{44}/\rho)^2(p + tg) - (c_{44}/\rho)^3(r + sf + tg) = 0$$

where $p = 3 + 2(\sigma + \xi)$

$r = \sigma + \xi + 1$

$s = \sigma^2(\sigma + 3\xi)/4$

$t = \sigma(\sigma + 2\xi)$

Therefore $M = (c_{44}/\rho)^2(p + tg)$

$N = (c_{44}/\rho)^3(r + sf + tg)$

Finally,

$$(7)\qquad \int (M/N)^{3/2} d\Omega = (\rho/c_{44})^{3/2}\int\left(\frac{p + tg}{r + sf + tg}\right)^{3/2} d\Omega$$

APPENDIX B. General Expressions for $(\partial^n I)/(\partial f^p \partial g^q)$

Writing $I = (P/Q)^{3/2}$, where

$P = a - g$, and

$Q = c + df - g$,

we have for the general expressions for $(\partial^n I)/(\partial f^p \partial g^q)$:

$$\frac{\partial I}{\partial f} = -\frac{3}{2}\frac{P^{3/2}d}{Q^{5/2}}$$

$$\frac{\partial I}{\partial g} = \frac{3}{2}\frac{P^{3/2}}{Q^{5/2}} - \frac{3}{2}\frac{P^{1/2}}{Q^{3/2}}$$

$$\frac{\partial^2 I}{\partial f^2} = \frac{15}{4}\frac{P^{3/2}d^2}{Q^{7/2}}$$

$$\frac{\partial^2 I}{\partial f \partial g} = -\frac{15}{4}\frac{P^{3/2}d}{Q^{7/2}} + \frac{9}{4}\frac{P^{1/2}d}{Q^{5/2}}$$

$$\frac{\partial^2 I}{\partial g^2} = \frac{15}{4}\frac{P^{3/2}}{Q^{7/2}} - \frac{9}{2}\frac{P^{1/2}}{Q^{5/2}} + \frac{3}{4}\frac{P^{-1/2}}{Q^{3/2}}$$

$$\frac{\partial^3 I}{\partial f^3} = -\frac{105}{8}\frac{P^{3/2}d^3}{Q^{9/2}}$$

$$\frac{\partial^3 I}{\partial f^2 \partial g} = \frac{105}{8}\frac{P^{3/2}d^2}{Q^{9/2}} - \frac{48}{8}\frac{P^{1/2}d^2}{Q^{7/2}}$$

$$\frac{\partial^3 I}{\partial f \partial g^2} = -\frac{105}{8}\frac{P^{3/2}d}{Q^{9/2}} + \frac{45}{4}\frac{P^{1/2}d}{Q^{7/2}} - \frac{9}{8}\frac{P^{-1/2}d}{Q^{5/2}}$$

$$\frac{\partial^3 I}{\partial g^3} = \frac{105}{8}\frac{P^{3/2}}{Q^{9/2}} - \frac{135}{8}\frac{P^{1/2}}{Q^{7/2}} + \frac{27}{8}\frac{P^{-1/2}}{Q^{5/2}} + \frac{3}{8}\frac{P^{-3/2}}{Q^{3/2}}$$

$$\frac{\partial^4 I}{\partial f^4} = \frac{945}{16}\frac{P^{3/2}d^4}{Q^{11/2}}$$

$$\frac{\partial^4 I}{\partial f^3 \partial g} = -\frac{945}{16}\frac{P^{3/2}d^3}{Q^{11/2}} + \frac{315}{16}\frac{P^{1/2}d^3}{Q^{9/2}}$$

$$\frac{\partial^4 I}{\partial f^2 \partial g^2} = \frac{945}{16}\frac{P^{3/2}d^2}{Q^{11/2}} - \frac{315}{8}\frac{P^{1/2}d^2}{Q^{9/2}} + \frac{45}{16}\frac{P^{-1/2}d^2}{Q^{7/2}}$$

$$\frac{\partial^4 I}{\partial f \partial g^3} = -\frac{945}{16}\frac{P^{3/2}d}{Q^{11/2}} + \frac{945}{16}\frac{P^{1/2}d}{Q^{9/2}} - \frac{135}{16}\frac{P^{-1/2}d}{Q^{7/2}} - \frac{9}{16}\frac{P^{-3/2}d}{Q^{5/2}}$$

$$\frac{\partial^4 I}{\partial g^4} = \frac{945}{16}\frac{P^{3/2}}{Q^{11/2}} - \frac{315}{4}\frac{P^{1/2}}{Q^{9/2}} + \frac{45}{4}\frac{P^{-1/2}}{Q^{7/2}} + \frac{9}{4}\frac{P^{-3/2}}{Q^{5/2}} + \frac{9}{16}\frac{P^{-5/2}}{Q^{3/2}}$$

$$\frac{\partial^5 I}{\partial f^5} = -\frac{10395}{32}\frac{P^{3/2}d^5}{Q^{13/2}}$$

$$\frac{\partial^5 I}{\partial f^4 \partial g} = \frac{10395}{32}\frac{P^{3/2}d^4}{Q^{13/2}} - \frac{2835}{32}\frac{P^{1/2}d^4}{Q^{11/2}}$$

$$\frac{\partial^5 I}{\partial f^3 \partial g^2} = -\frac{10395}{32}\frac{P^{3/2}d^3}{Q^{13/2}} + \frac{2835}{16}\frac{P^{1/2}d^3}{Q^{11/2}} - \frac{315}{32}\frac{P^{-1/2}d^3}{Q^{9/2}}$$

$$\frac{\partial^5 I}{\partial f^2 \partial g^3} = \frac{10395}{32}\frac{P^{3/2}d^2}{Q^{13/2}} - \frac{8505}{32}\frac{P^{1/2}d^2}{Q^{11/2}} + \frac{945}{32}\frac{P^{-1/2}d^2}{Q^{9/2}} + \frac{45}{32}\frac{P^{-3/2}d^2}{Q^{7/2}}$$

$$\frac{\partial^5 I}{\partial f \partial g^4} = -\frac{10395}{32}\frac{P^{3/2}d}{Q^{13/2}} + \frac{2835}{8}\frac{P^{1/2}d}{Q^{11/2}} - \frac{315}{8}\frac{P^{-1/2}d}{Q^{9/2}} - \frac{45}{8}\frac{P^{-3/2}d}{Q^{7/2}} - \frac{27}{32}\frac{P^{-5/2}d}{Q^{5/2}}$$

$$\frac{\partial^5 I}{\partial g^5} = \frac{10395}{32}\frac{P^{3/2}}{Q^{13/2}} - \frac{14175}{32}\frac{P^{1/2}}{Q^{11/2}} + \frac{315}{4}\frac{P^{-1/2}}{Q^{9/2}} + \frac{45}{4}\frac{P^{-3/2}}{Q^{7/2}} + \frac{135}{32}\frac{P^{-5/2}}{Q^{5/2}} + \frac{45}{32}\frac{P^{-7/2}}{Q^{3/2}}$$

APPENDIX C. Table of Factors Used in Calculating $\int I \, d\Omega$ by Method II.

(a) Iron

cos θ	W	X	Y	Z
0.0	1.33133	-0.25000	0.53479	-0.25000
0.1	1.32143	-0.24503	0.52489	-0.24020
0.2	1.29293	-0.23040	0.49639	-0.21224
0.3	1.24943	-0.20703	0.45289	-0.17033
0.4	1.19693	-0.17640	0.40039	-0.12081
0.5	1.14383	-0.14063	0.34729	-0.071381
0.6	1.10093	-0.10240	0.30439	-0.029794
0.7	1.08143	-0.065025	0.28489	-0.0022707
0.8	1.10093	-0.03240	0.30439	0.0084396
0.9	1.17743	-0.009025	0.38089	0.0053728
1.0	1.33133	0.000000	0.53479	0.0000000

(b) Silver

cos θ	W	X	Y	Z
0.0	1.03543	-0.25000	0.43797	-0.25000
0.1	1.02553	-0.24503	0.42807	-0.23979
0.2	0.99703	-0.23040	0.39957	-0.21070
0.3	0.95353	-0.20703	0.35607	-0.16719
0.4	0.90103	-0.17640	0.30357	-0.11606
0.5	0.84793	-0.14063	0.25047	-0.065469
0.6	0.80503	-0.10240	0.20757	-0.023593
0.7	0.78553	-0.065025	0.18807	0.0030900
0.8	0.80503	-0.03240	0.20757	0.011928
0.9	0.88153	-0.009025	0.28407	0.0066027
1.0	1.03543	0.000000	0.43797	0.0000000

(c) Copper

cos θ	W	X	Y	Z
0.0	1.0306	-0.25000	0.42197	-0.25000
0.1	1.0207	-0.24503	0.41207	-0.23938
0.2	0.99219	-0.23040	0.38357	-0.20916
0.3	0.94869	-0.20703	0.34007	-0.16407
0.4	0.89619	-0.17640	0.28757	-0.11134
0.5	0.84309	-0.14063	0.23447	-0.059586
0.6	0.80019	-0.10240	0.19157	-0.017424
0.7	0.78069	-0.065025	0.17207	0.008419
0.8	0.80019	-0.03240	0.19157	0.015398
0.9	0.87669	-0.009025	0.26807	0.007826
1.0	1.0306	0.000000	0.42197	0.000000

(d) Lead

cos θ	W	X	Y	Z
0.0	0.82397	-0.25000	0.35955	-0.25000
0.1	0.81407	-0.24503	0.34965	-0.23908
0.2	0.78557	-0.23040	0.32115	-0.20803
0.3	0.74207	-0.20703	0.27765	-0.16180
0.4	0.68957	-0.17640	0.22515	-0.10790
0.5	0.63647	-0.14063	0.17205	-0.055299
0.6	0.59357	-0.10240	0.12915	-0.012931
0.7	0.57407	-0.06503	0.10965	0.012303
0.8	0.59357	-0.03240	0.12915	0.017925
0.9	0.67007	-0.00903	0.20565	0.0087167
1.0	0.82397	0.00000	0.35955	0.0000000

APPENDIX D(a)Use of Elliptic Functions to Evaluate J

(a) The three fundamental elliptic integrals are:

(1) Normal elliptic integral of the first kind,

$$\int_0^y \frac{dt}{\sqrt{(1-t^2)(1-k^2t^2)}} = \int_0^{\varphi} \frac{d\gamma}{\sqrt{1-k^2\sin^2\gamma}}$$

$$= \int_0^{u_1} du = u_1 \equiv \mathrm{sn}^{-1}(y,k) \equiv F(\varphi,k)$$

$$(y = \sin\varphi; \quad \varphi = \mathrm{am}\, u_1)$$

(2) Normal elliptic integral of the second kind,

$$\int_0^y \sqrt{\frac{1-k^2t^2}{1-t^2}}\, dt = \int_0^{\varphi} \sqrt{1-k^2\sin^2\gamma}\, d\gamma = \int_0^{u_1} \mathrm{dn}^2 u\, du$$

$$\equiv E(u_1) \equiv E(\mathrm{am}\, u_1,k) \equiv E(\varphi,k)$$

(3) Normal elliptic integral of the third kind,

$$\int_0^y \frac{dt}{(1-\alpha^2t^2)\sqrt{(1-t^2)(1-k^2t^2)}} = \int_0^{\varphi} \frac{d\gamma}{(1-\alpha^2\sin^2\gamma)\sqrt{1-k^2\sin^2\gamma}}$$

$$= \int_0^{u_1} \frac{du}{1-\alpha^2\mathrm{sn}^2 u} = \Pi(u_1,\alpha^2) \equiv \Pi(\mathrm{am}\, u_1,\alpha^2,k) \equiv \Pi(\varphi,\alpha^2,k)$$

$$(-\infty < \alpha^2 < \infty)$$

When y =1, the integrals are said to be complete. In that case, one writes:

(1) $$\int_0^{\pi/2} \frac{d\gamma}{\sqrt{1-k^2\sin^2\gamma}} = \int_0^K du = F(\pi/2,k) \equiv K(k) \equiv K$$

(2) $$\int_0^{\pi/2} \sqrt{1-k^2\sin^2\gamma}\, d\gamma = \int_0^K \mathrm{dn}^2 u\, du = E(\pi/2,k) \equiv E(k) \equiv E$$

(3) $$\int_0^{\pi/2} \frac{d\gamma}{(1-\alpha^2\sin^2\gamma)\sqrt{1-k^2\sin^2\gamma}} = \int_0^K \frac{du}{1-\alpha^2\mathrm{sn}^2 u} = \Pi(\pi/2,\alpha^2,k) \equiv \Pi(\alpha^2,k)$$

$$[\alpha^2 \neq 1]$$

APPENDIX D(b). Use of Elliptic Functions to Evaluate J

(b) Integration

I. $n_2^2 < 0$

$$J = \int_0^{\pi/2} \left(\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma} \right)^{3/2} d\gamma$$

$$= \int_0^{\pi/2} \frac{d\gamma}{(1 + |n_2^2| \sin^2\gamma)^{3/2}} - \frac{3}{2} n_1^2 \int_0^{\pi/2} \frac{\sin^2\gamma \, d\gamma}{(1 + |n_2^2| \sin^2\gamma)^{3/2}}$$

(See p. 33-34 for validity of this expansion of numerator).

$$= k'E + 3 n_1^2 \frac{d}{d|n_2^2|} \int_0^{\pi/2} \frac{d\gamma}{(1 + |n_2^2| \sin^2\gamma)^{1/2}}$$

$$= k'E + 3 n_1^2 \frac{d}{d|n_2^2|} (k'K)$$

$$= k'E + \frac{3}{2} \frac{n_1^2}{|n_2^2|} k'(E - k'^2 K) - \frac{3}{2} n_1^2 k'^3 K$$

$$= k'E + \frac{3}{2} \frac{n_1^2 k'^3}{k^2} (E - k'^2 K) - \frac{3}{2} n_1^2 k'^3 K$$

where $\quad k^2 = 1 - k'^2 = \dfrac{|n_2^2|}{1 + |n_2^2|}$

II. $1 > n_1^2 > n_2^2 > 0$

$$J = \int_0^{\pi/2} \frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}} \, d\gamma$$

$$= \int_0^{\pi/2} \frac{d\gamma}{1 - n_2^2 \sin^2\gamma} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}} - n_1^2 \int_0^{\pi/2} \frac{\sin^2\gamma \, d\gamma}{1 - n_2^2 \sin^2\gamma} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}}$$

$$= gE - 2 n_1^2 \frac{\partial}{\partial n_2^2} \int_0^{\pi/2} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}} \, d\gamma$$

$$= gE - 2n_1^2 \frac{\partial}{\partial n_2^2} \int_0^{\pi/2} \frac{d\gamma}{\sqrt{(1 - n_1^2 \sin^2\gamma)(1 - n_2^2 \sin^2\gamma)}}$$

$$+ 2n_1^4 \frac{\partial}{\partial n_2^2} \int_0^{\pi/2} \frac{\sin^2\gamma \, d\gamma}{\sqrt{(1 - n_1^2 \sin^2\gamma)(1 - n_2^2 \sin^2\gamma)}}$$

$$= gE - 2n_1^2 \frac{\partial}{\partial n_2^2} (gK) + 2n_1^4 \frac{\partial}{\partial n_2^2} g \int_0^K \frac{\mathrm{sn}^2 u \, du}{1 - n_2^2 + n_2^2 \,\mathrm{sn}^2 u}$$

$$= gE - \frac{n_1^2 (K - E) g^3}{k^2} + 2n_1^4 \frac{\partial}{\partial n_2^2} g^3 \int_0^K \frac{\mathrm{sn}^2 u \, du}{1 - \alpha^2 \,\mathrm{sn}^2 u}$$

where $\alpha = -\dfrac{n_2^2}{1 - n_2^2}$

$$= gE - \frac{n_1^2 g^3}{k^2} (K - E) + 2n_1^4 \frac{\partial}{\partial n_2^2} g^3 \left[\frac{K}{k^2 - \alpha^2} - \frac{\pi}{2} \frac{\Lambda_0(\psi, k)}{\sqrt{\alpha^2 (1 - \alpha^2)(\alpha^2 - k^2)}} \right]$$

$$= gE - \frac{n_1^2 g^3}{k^2} (K - E) + 2n_1^4 \frac{\partial}{\partial n_2^2} \left[\frac{Kg}{n_1^2} - \frac{\pi}{2} \frac{\Lambda_0(\psi, k)}{n_1 n_2} \right]$$

$$= gE - \frac{n_1^2 g^3}{k^2} (K - E) + \frac{n_1^2 g^3}{k^2} (K - E) + \frac{\pi}{2} \frac{n_1^3}{n_2^3} \Lambda_0(\psi, k) - \frac{n_1^2 g E}{n_2^2}$$

$$= gE - \frac{n_1^2}{n_2^2} \left[gE - \frac{n_1}{n_2} \frac{\pi}{2} \Lambda_0(\psi, k) \right]$$

where $k^2 = \dfrac{n_1^2 - n_2^2}{1 - n_2^2}$; $g^2 = \dfrac{1}{1 - n_2^2}$; $\psi = \sin^{-1} \dfrac{n_2}{n_1}$

III. $1 > n_2^2 > n_1^2 > 0$

$$J = \int_0^{\pi/2} \frac{d\gamma}{1 - n_2^2 \sin^2\gamma} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}} - n_1^2 \int_0^{\pi/2} \frac{\sin^2\gamma \, d\gamma}{1 - n_2^2 \sin^2\gamma} \sqrt{\frac{1 - n_1^2 \sin^2\gamma}{1 - n_2^2 \sin^2\gamma}}$$

$$= g\int_0^K \mathrm{nd}^2 u\, du - 2n_1^2 \frac{\partial}{\partial n_2^2}\int_0^{\pi/2} \frac{d\gamma}{\sqrt{(1-n_1^2\sin^2\gamma)(1-n_2^2\sin^2\gamma)}}$$

$$+ 2n_1^4 \frac{\partial}{\partial n_2^2}\int_0^{\pi/2} \frac{\sin^2\gamma\, d\gamma}{\sqrt{(1-n_1^2\sin^2\gamma)(1-n_2^2\sin^2\gamma}}$$

$$= \frac{gE}{k'^2} - 2n_1^2 \frac{\partial}{\partial n_2^2}(gK) + 2n_1^4 \frac{\partial}{\partial n_2^2}\, g\int_0^K \frac{\mathrm{sn}^2 u\, du}{1-n_1^2+n_1^2\,\mathrm{sn}^2 u}$$

$$= \frac{gE}{k'^2} - \frac{n_1^2 g^3(E-k'^2K)}{k^2k'^2} + 2n_1^4 g \frac{\partial}{\partial n_2^2}\ \frac{1}{1-n_1^2}\int_0^K \frac{\mathrm{sn}^2 u\, du}{1-\alpha^2\,\mathrm{sn}^2 u}$$

where $\alpha^2 = -\dfrac{n_1^2}{1-n_1^2}$

$$= \frac{gE}{k'^2} - \frac{n_1^2 g^3(E-k'^2K)}{k^2k'^2} + 2n_1^4 g^3 \frac{\partial}{\partial n_2^2}\left[\frac{K}{k^2-\alpha^2} - \frac{\pi}{2}\,\frac{\Lambda_0(\psi,k)}{\sqrt{\alpha^2(1-\alpha^2)(\alpha^2-k^2}}\right.$$

$$= \frac{gE}{k'^2} - \frac{n_1^2 g^3(E-k'^2K)}{k^2k'^2} + 2n_1^4 g \frac{\partial}{\partial n_2^2}\left(\frac{K}{n_2^2}\right) - \pi n_1^3 \frac{\partial}{\partial n_2^2}\left(\frac{\Lambda_0(\psi,k)}{n_2}\right)$$

$$= \frac{gE}{k'^2} - \frac{n_1^2 g^3(E-k'^2K)}{k^2k'^2} + \frac{n_1^4 g^3}{n_2^2}\left(\frac{E-k'^2K}{k^2k'^2}\right) - \frac{n_1^4 gK}{n_2^4} + \frac{\pi n_1^3\Lambda_0(\psi,k)}{2n_2^3}$$

$$= \frac{gE}{k'^2} - n_1^2 g^3\left(1-\frac{n_1^2}{n_2^2}\right)\left(\frac{E-k'^2K}{k^2k'^2}\right) - \frac{n_1^4 gK}{n_2^4} + \frac{\pi n_1^3\Lambda_0(\psi,k)}{2n_2^3}$$

$$= \frac{gE}{k'^2} - \frac{n_1^2 g}{n_2^2}\left(\frac{E-k'^2K}{k^2k'^2}\right) - \frac{n_1^4 gK}{n_2^2} + \frac{\pi n_1^3\Lambda_0(\psi,k)}{2n_2^3}$$

$$= \frac{k^2}{n_2^2 g}\left(\frac{E}{k'^2} + \frac{n_1^2K}{n_2^2}\right) + \frac{\pi}{2}\,\frac{n_1^3}{n_2^3}\Lambda_0(\psi,k)$$

where $k^2 = 1-k'^2 = \dfrac{n_2^2-n_1^2}{1-n_1^2}$; $g^2 = \dfrac{1}{1-n_1^2}$; $\psi = \sin^{-1}\dfrac{n_1}{n_2}$

$$\Lambda_0(\psi,k) = \frac{2}{\pi}\left[EF(\psi,k') + KE(\psi,k') - KF(\psi,k')\right]$$

APPENDIX E. $\int I d\Omega$ by Method III

(a) Silver

$\cos\theta$	n_1^2	n_2^2	k^2	K	E	ψ	$\Lambda_0(\psi,k)$	$(W/Y)^{3/2}$	$\frac{1}{2\pi}\int_0^{2\pi} I\, d\varphi$
0.0	0.24145	0.57082	0.43421	1.8021	1.3830	40°34.2'	0.57807	3.6352	5.4945
0.1	0.23893	0.56017	0.42209	1.7932	1.3887	40°46.5'	0.58263	3.7081	5.5174
0.2	0.23109	0.52732	0.38526	1.7675	1.4063	41°27.1'	0.59722	3.9415	5.6051
0.3	0.21712	0.46954	0.32242	1.7271	1.4353	42°50.7'	0.62497	4.3821	5.8052
0.4	0.19578	0.38232	0.23195	1.6758	1.4753	45°41.5'	0.67436	5.1134	6.1855
0.5	0.16585	0.26138	0.11452	1.6189	1.5248	52°48.2'	0.77424	6.2287	6.7997
0.6	0.12720	0.11366	0.015276	1.5769	1.5648	70°57.7'	0.94157	7.6380	7.5514
0.7	0.082779	-0.016430	0.016164	1.5772	1.5644			8.5361	7.9113
0.8	0.040247	-0.057465	0.054342	1.5929	1.5492			5.8477	7.6380
0.9	0.010238	-0.023243	0.022715	1.5798	1.5618			5.4666	5.3323
1.0	0.000000	0.000000	0.000000	1.5708	1.5708			3.6352	3.6351

(b) Copper

$\cos\theta$	n_1^2	n_2^2	k^2	K	E	ψ	$\Lambda_0(\psi,k)$	$(W/Y)^{3/2}$	$\frac{1}{2\pi}\int_0^{2\pi} I \, d\varphi$
0.0	0.24258	0.59246	0.46194	1.8231	1.3696	39°47.0'	0.56376	3.8168	5.9917
0.1	0.24006	0.58092	0.44854	1.8128	1.3761.	40°00.2'	0.56880	3.8983	6.0089
0.2	0.23221	0.54530	0.40778	1.7830	1.3957	40°44.1'	0.58465	4.1602	6.0835
0.3	0.21823	0.48246	0.33799	1.7368	1.4282	42°15.9'	0.61528	4.6594	6.2793
0.4	0.19683	0.38718	0.23700	1.6788	1.4731	45°28.8'	0.67102	5.5015	6.6874
0.5	0.16680	0.25413	0.10481	1.6145	1.5288	54°06,6'	0.78930	6.8183	7.3842
0.6	0.12797	0.090954	0.040724	1.5872	1.5547	57°28.0'	0.83460	8.5368	8.2835
0.7	0.083292	-0.048928	0.046646	1.5897	1.5523			9.6639	8.7519
0.8	0.040490	-0.080378	0.074398	1.6014	1.5412			8.5368	7.8204
0.9	0.010294	-0.029194	0.028366	1.5821	1.5596			5.9143	5.7441
1.0	0.000000	0.000000	0.000000	1.5708	1.5708			3.8168	3.8169

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(c) Lead

$\cos\theta$	n_1^2	n_2^2	k^2	K	E	ψ	$\Lambda_0(\psi,k)$	$(W/Y)^{3/2}$	$\frac{1}{2\pi}\int_0^{2\pi} I\,d\varphi$
0.0	0.30341	0.69531	0.56260	1.9111	1.3184	$41^\circ 20.6'$	0.56431	3.4692	6.3038
0.1	0.30099	0.68376	0.54759	1.8966	1.3262	$41^\circ 34.0'$	0.56872	3.5525	6.2939
0.2	0.29329	0.64777	0.50159	1.8555	1.3498	$42^\circ 17.4'$	0.58670	3.8258	6.3094
0.3	0.27898	0.58276	0.42132	1.7926	1.3892	$43^\circ 46.9'$	0/61867	4.3694	6.4598
0.4	0.25581	0.47924	0.30023	1.7140	1.4453	$46^\circ 56.3'$	0.67651	5.3599	6.9102
0.5	0.22095	0.32141	0.12895	1.6254	1.5188	$56^\circ 00.5'$	0.80319	7.1151	7.8460
0.6	0.17252	0.10012	0.080455	1.6039	1.5387	$49^\circ 37.4'$	0.74656	9.8530	9.2810
0.7	0.11327	-0.11220	0.10088	1.6128	1.5304			11.979	11.6428
0.8	0.05459	-0.13879	0.12187	1.6222	1.5218			9.8530	8.5971
0.9	0.01347	-0.04239	0.040666	1.5871	1.5547			5.8815	5.6449
1.0	0.00000	0.00000	0.000000	1.5708	1.5708			3.4692	3.4692

(d) Potassium

$\cos\theta$	n_1^2	n_2^2	k^2	K	E	ψ	$\Lambda_0(\psi,k)$	$(W/Y)^{3/2}$	$\frac{1}{2\pi}\int_0^{2\pi} I\,d\varphi$
0.0	0.29082	0.74600	0.64184	1.9976	1.2753	38°38.2'	0.51745	4.1084	8.7403
0.1	0.28835	0.73150	0.62271	1.9749	1.2860	38°53.5'	0.52408	4.2233	8.6319
0.2	0.28055	0.68614	0.56375	1.9122	1.3178	39°45.0'	0.54526	4.6048	8.4244
0.3	0.26618	0.60353	0.45972	1.8214	1.3706	41°36.9'	0.58614	5.3828	8.3926
0.4	0.24323	0.46979	0.29938	1.7136	1.4456	46°01.0'	0.66613	6.8682	8.8563
0.5	0.20922	0.25980	0.063962	1.5969	1.5464	63°49.0'	0.88351	9.7156	10.1808
0.6	0.16273	-0.046221	0.044179	1.5886	1.5533			14.730	12.5325
0.7	0.10664	-0.32462	0.24507	1.6831	1.4696			19.139	14.4444
0.8	0.051490	-0.26664	0.21051	1.6650	1.4845			14.730	11.9334
0.9	0.012788	-0.067549	0.063275	1.5966	1.5456			7.6852	7.2502
1.0	0.000000	0.000000	0.000000	1.5708	1.5708			4.1084	4.1084

(e) Sodium

$\cos\theta$	n_1^2	n_2^2	k^2	K	E	ψ	$\Lambda_0(\psi,k)$	$(W/Y)^{3/2}$	$\frac{1}{2\pi}\int_0^{2\pi} I\,d\varphi$
0.0	0.31403	0.81585	0.73155	2.1247	1.2225	38°20.8'	0.49659	4.1875	11.1353
0.1	0.31166	0.80039	0.71001	2.0904	1.2357	38°36 6'	0.50406	4.3171	10.7949
0.2	0.30408	0.75178	0.64332	1.9994	1.2745	39°29.6'	0.52739	4.7529	10.1100
0.3	0.28987	0.66180	0.52375	1.8747	1.3385	41°26.3'	0.57255	5.6730	9.6889
0.4	0.26659	0.51086	0.33306	1.7337	1.4304	46°15.1'	0.66280	7.5436	10.0611
0.5	0.23107	0.25536	0.03159	1.5834	1.5585	72°02.1'	0.94404	11.576	11.8388
0.6	0.18102	-0.17374	0.14802	1.6343	1.5109			20.295	15.7185
0.7	0.11905	-0.61738	0.38172	1.7651	1.4079			30.033	19.6127
0.8	0.05728	-0.42920	0.30031	1.7141	1.4452			20.295	15.0013
0.9	0.01405	-0.09114	0.08353	1.6053	1.5375			8.6391	8.0127
1.0	0.00000	0.00000	0.00000	1.5708	1.5708			4.1875	4.1875

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